EXHIBIT A

MOLECULAR CRYSTALS
AND
LIQUID CRYSTALS

SUPPLEMENT SERIES.

ALIGNMENT OF NEMATIC LIQUID CRYSTALS AND THEIR MIXTURES

Jacques Cognard

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Primarily fundamental in tenor, MCLC publishes original research papers of both an experimental and theoretical nature in three areas of specialization: molecular crystals (spectroscopy, energy and charge transfer, solid state reactions, photo and radiation effects); low dimensional solids (structure, electronic, magnetic, and optical properties, transport mechanisms); and liquid crystals (electro and magneto-optical phenomena, thermodynamics, phase transitions, structure, NMR and orientation controlled spectroscopy). In all three areas, experimental manuscripts describing both preparation and properties will be considered. The above listing of topics is meant to be purely illustrative of typical subject matter.

ALIGNMENT OF NEMATIC LIQUID CRYSTALS AND THEIR MIXTURES

MOLECULAR CRYSTALS AND LIQUID CRYSTALS,
SUPPLEMENT SERIES.

SUPPLEMENT 1

Alignment of Nematic Liquid Crystals and Their Mixtures

by

JACQUES COGNARD

Chemistry Group, ASULAB S.A., Neuchâtel, Switzerland

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
SUPPLEMENT SERIES

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SUPPLEMENT 1

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and Their Mixtures **by Jacques Cognard**

Additional volumes in preparation.

Preface

Research in the field of Molecular and Liquid Crystals has reached a certain degree of maturity. It was considered timely, therefore, to inaugurate a supplement series to the journal of *Molecular Crystals and Liquid Crystals.* The aim of this series is to provide in-depth reviews, in the form of monographs, of specific topics within this wide and rapidly growing field. As a result of expansion and diversification, regular research articles must be highly specialized. It is important, therefore, to provide the mechanism whereby researchers, students and practitioners can readily obtain a balanced view of the important results in various areas of the overall field. This is the aim of this new supplement series.

G. J. Dienes
Managing Editor

Alignment of Nematic Liquid Crystals and Their Mixtures

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INTRODUCTION

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The most recent reviews concerning the alignment of liquid crystals (LC) appeared five years ago.[1-3] Since then studies of LC alignment have proceeded actively: the tangential evaporation of oxides and fluorides has found wide industrial acceptance: aligning properties of layers deposited in various ways have been well documented and studies of LC surface interactions are numer-

ous. Many methods of aligning LCs have been described but attempts to utilize or even reproduce published results are often discouraging.

It is the purpose of this paper to review the various methods described, to extend them to other commercial LC mixtures and point out the most reliable ones, as found through our own experience in developing displays for electronic watches.

We have sought to be comprehensive up to December 1979 and cite any English, French or German references available to us through computer search, abstracts bibliography and cross referencing. It was thus impossible to cover all studies and we considered only the most practical methods of LC alignment compatible with practical requirements. We insist on those processes that give reproducible results.

An evaluation of an alignment process has to consider its reproducibility, applicability to various LCs, lifetime and compatibility with the associated

LC Code

(I) LC commercial mixtures

(from our chromatographic analysis)

Code	Composition	T_{NI} °C	Source
Zli 1132	0.15 BCH–5 : 0.24 PCH – 3 : 0.36 PCH–5 0.25 PCH–7	70	Merck
E 3	0.55 K15: 0.14 M15: 0.13 M21: 0.18 M24	54.3	BDH
E 7	0.51 K15: 0.25 K 21: 0.16 M 24: 0.08 T15	59.8	BDH
E 8	0.45 K15 : 0.16 M9 : 0.12 M15 : 0.16 M 24 0.11 T 15	70.5	BDH
ROTN 103	0.05 PEPN 4 : 0. 24 PEPN 5 : 0.13 PEPN 6 0.18 PEPN 7 : 0.12 P₃ 5 : 0.08 P₃ 7 : 0.20 T P₃ 4	81.4	Roche
ROTN 200	0.33 S3 : 0. 67 S 6	65.2	Roche
ROTN 404	0.31 M 15 : 0.14 M 24 : 0.14 T 15 : 0.09 P₃ 5 0.18 P₃ 7 : 0.14 T P₃ 4	105	Roche

sealing process. Sealing of LC displays involves either a high temperature (500°C) glass frit technique or adhesives cured around 200°C.

Most alignment methods have been tested on MBBA,† a very sensitive Schiff's base LC, while biphenyls, esters or phenylcyclohexane eutectic mixtures are of current industrial interest. Our evaluations considered the commercial mixtures ROTN 200, ROTN 103, ROTN 404, E7, E8 and Zli 1132.† On filling a cell, the nematic director generally aligns in the direction of flow (4a), but the resulting orientation is temperature sensitive (4b). Heating the LC to its isotropic phase will often promote a uniform alignment, and slow

LC Code

(2) LCs of current industrial use

C B 15	NC—◯—◯—CH(CH₃)CH₂—C₂H₅	PCH-5	NC—◯—◯H—C₅H₁₁
S 3	NC—◯—N=CH—◯—C₅H₁₁	PCH-7	NC—◯—◯H—C₇H₁₅
S 6	NC—◯—N=CH—◯—C₆H₁₃	HPE-33	H₇C₃—◯—COO—C₃H₇
K-15	NC—◯—◯—C₅H₁₁	HPEH-23	H₅C₂—◯—◯—COO—C₃H₇
K-21	NC—◯—◯—C₂H₅	HPEH-43	H₉C₄—◯—◯—COO—C₃H₇
M-9	NC—◯—◯—OC₃H₇	PEPN 4	NC—◯—OOC—◯—C₄H₉
M-15	NC—◯—◯—OC₅H₁₁	PEPN 5	NC—◯—OOC—◯—C₅H₁₁
M-21	NC—◯—◯—OC₆H₁₃	PEPN 6	NC—◯—OOC—◯—C₆H₁₃
M-24	NC—◯—◯—OC₇H₁₅	PEPN 7	NC—◯—OOC—◯—C₇H₁₅
T-15	NC—◯—◯—◯—C₅H₁₁	P₃5	NC—◯—◯=C—◯—C₅H₁₁
BCH-5	NC—◯—◯—◯H—C₅H₁₁	P₃7	NC—◯—◯=C—◯—C₇H₁₅
PCH-3	NC—◯—◯H—◯—C₃H₇	TP₃4	NC—◯—◯—◯—C₅H₁₁

† See LC code.

(3) Abbreviations used in the text

Azo	LCs with an azo linkage	R—◯—N=N—◯—R'
Azoxys (A)	LCs with azoxy linkage	R—◯—N=N→O—◯—R'

Azoxys eut. mixt.   Azoxys eutectic mixture
BAB   4,4'-Bis(n-butoxyl)azoxybenzene
BBCA   4-Butoxybenzylidene-4'-cyanoaniline (pSB)
BECS   4-n-Butyl-4'-ethoxy-α-chlorostilbene

CB	Cyanobiphenyls	C_nH_{2n+1}—◯—◯—C≡N (XCB)
CBOA	4-Cyanobenzylidene-4'-n-octylaniline	C_nH_{2n+1}—◯—O—◯—C≡N (XOCB)

CE   Cyano esters
CN   Cholesteryl nonanoate
DIBAB   4,4'-Di-n-butylazoxybenzene
Δε   Dielectric anisotropy

Esters	LCs with an ester linkage	R—◯—COO—◯—R'

MBAB   4-Methoxy-4'-butylazoxybenzene
MBBA   4-Methoxybenzylidene-4'-n-butylaniline (nSB)
MPT   4-Methoxy-4'-pentyltolan
n   Negative dielectric anisotropy (Δε < 0)
OCB   Alkoxycyanobiphenyls
p   Positive dielectric anisotropy (Δε > 0)
PAA   Para-azoxyanisole
PAP   Para-azoxyphenetol (4,4'-ethoxyazoxybenzene)

PCH	Phenylcyclohexane	R—◯—◯H—R'

p Esters mixt.   Mixture of positive LC esters
PHT   4-Propyloxy-4'-heptyltolans

SB	LCs with a Schiff base linkage	R—◯—CH=N—◯—R'
Stilbenes (S)	LCs with a double bond linkage	R—◯—C=C—◯—R'
Tolans (T)	LCs with a triple bond linkage	R—◯—C≡C—◯—R'

cooling also favors the LC alignment but such tricks characterize a weak aligning mechanism with reproducibility not guaranteed.

For practical purpose a good aligning process has to produce a uniform alignment immediately on filling the cell. In the case of weak effects the real cause of alignment may not be the supposed mechanism.

I A CRITICAL REVIEW OF THE LITERATURE

I.I The alignment of liquid crystals on smooth surfaces

I.1.1 Inorganic Substrates

The surfaces of glasses, oxides and metals exhibit an aligning influence on liquid crystals (Table I). The reproducibility and uniformity of this type of alignment is poor as the substrate surface is ill defined. The cleaning procedures employed in the substrate preparation also play a role, e.g., MBBA molecules will align perpendicular to the surface (homeotropically) of acid treated glasses[5] or oxides,[6,7] but nonuniform alignment parallel† to the substrate surface is obtained with fired[5] or detergent cleaned glasses.[6,8] Homeotropic alignment on acid treated surfaces is limited to a few Schiff bases, and attempts to rationalize the alignment effect observed on 12 different LCs led to the hypotheses that it was due to a homeotropic aligning impurity,[7] as most polar molecules tend to induce perpendicular alignment (see paragraph 3). Recent investigations gave elegant evidence of the dramatic influence of impurities on LCs alignment in many compounds.[9] Boiling a glass plate in sulfuric acid is supposed to unpolish it, as does dipping in HF solution,[10] which may help homeotropic orientation, as observed with MBBA, however, acid washed glasses align azoxys parallel to the substrate.[10] Oxidation of SnO_2 or In_2O_3 coating in an oxygen plasma lead to layers causing parallel alignment of biphenyls.[25,26]

In Table I reported alignment effects of cleaved crystals and evaporated layers have been collected. One sees that, although some layers have been observed to induce homeotropic alignment of certain LCs, generally parallel alignment is observed. We have been unable to obtain reproducible homeotropic alignment using evaporated inorganic layers although it does occur sometimes. It has to be considered that reliable homeotropic alignment may not be obtained from such surfaces.

I.1.2 Organic polymers

Polymer coatings on glass substrates can be employed to align liquid crystals, but film uniformity and the substrate used influence the observed results.

† The terms "homogeneous and parallel" imply parallel uniform, and nonuniform alignment, respectively.

TABLE I

Alignment of nematic LCs on inorganic substrates[a]

I a	II a	III b	IV b	V b	VI b	VII b	VIII	I b	II b	III a	IV a	V a
LiF ⊥ 12	CaF₂ × 20 ⊥ 12									BN × 19	C × 6,20,24	
NaF × 11 NaCl × 20,90b	MgF₂ × 15,20,22 Mg(OH)₂ ⊥ 10 (Brucite)									Al × 17,20 Al₂O₃ × 17,20,21 ⊥ 13,14,20 Aluminosilicates: × 10,23	Si₃N₄ × 18 SiO₂ × 17,19,20	
KBr × 20,90b KI × 3			TiO₂ × 19 20 22		Cr₂O₃ × 21 Cr × 17	Fe₂O₃ ⊥ 16	NiO × 21 Ni × 47		ZnS × 21 ⊥ 13 ZnO × 11		Ge₂O₃ × 16	AsS₃ × 10,23 (Orpiment)
		Y₂O₃ × 19	ZrO₂ × 20 ⊥ 20							In₂O₃ × 17,20 ⊥ 17,20	SnO₂ × 6,7,20,21 ⊥ 6,7,20	
Cs₂O × 19	BaTiO₄ × 22	CeO₂ × 19 ThF₄ ⊥ 13		TaN₃ × ⊥ 16			Pt × 17,20	Au × 17,20	HgF₂ × 19		PbO₂ × 21	

[a] Often the same layer has been reported to induce either parallel or perpendicular alignment. Our investigations have generally shown the nematic orientation to be parallel to the surface. Impurities or surface hydrolysis may cause a homeotropic orientation of some LCs which is not characteristic of the surface. ⊥ = homeotropic alignment; × = parallel, nonuniform. Reference 20 to our work means that we have observed these alignments on our test LC mixtures.

TABLE II

Alignment of nematic LCs on organic polymers[*]

Polymer	Commercial name	Source	10^3 J m^{-2}	Mode of coating	Surface state	Liquid crystals	Alignment	Ref.
Polyalkenes								
p. ethylene	Supralhen Skyn	Kalle	28–36	Thick film	Natural	MBBA/TN200/E7/TN103	×	20
p. ethylene	Supralhen Skyn	Kalle	28–36	Thick film	Rubbed	MBBA/TN200/E7/TN103	∥	20
p. isobutene	...	...	27	Plasma polym.	Rubbed	MBBA/esters/tolanes	∥	34
p. butadiene	Polyoil 1300	Hüls	31, 33 (34)	Polym. sol.	Rubbed	n. Schiff base mixt.	∥	36
Polyacrylics								
p. acrylate	RE 377	Mitsubishi Rayon	35–42	Polym. sol.	Rubbed	n. Schiff base mixt.	∥	36
p. methyl methacrylate	...	...	33–44	Plasma polym.	Rubbed	MBBA/esters/tolanes	∥	34
p. cyanoacrylate	Ep I	Taoka Chem.	33–34, 37 (34)	Polym. sol.	Rubbed	n. Schiff base mixt.	∥	36
p. acrylonitrile	Barex	Wipf	44	Film	Natural	MBBA/TN103/E7	×	20
				Film	Rubbed	MBBA/TN103/E7	∥	20
Polyvinyls								
p. vinyl alcohol	Polyviol 13/140	Wackez	37	Polym. sol.	Rubbed	MBBA, azoxys. TN103, E7	∥	20
p. vinyl acetate	Vinyon	Nichia Paint	37	Polym. sol.	Rubbed	n. Schiff base mixt.	∥	36
p. vinyl butyral	Rhovinal B 20-30	Rhodia	24–32	Polym. sol.	Rubbed	MBBA, azoxys. TN103, E7	∥	20
p. vinyl chloride	Genotherm	Kalle	39	Film	Natural	MBBA, azoxys. TN103, E7	×	20
p. vinyl chloride	Genotherm	Kalle	39	Film	Rubbed	MBBA, azoxys. TN103, E7	∥	20
p. vinyl pyridinium	...	...	...	Polym. sol.	Natural	5CB: 80CB	⊥	120
Polystyrenes								
p. styrene	Styrite	Daido Kogyo	27–33	Polym. sol.	Rubbed	MBBA/esters/tolanes/CB	∥	36
p. styrene	...	...	...	Sol. p. styrene + divinyl benzene	Rubbed	Schiff base mixt./5CB	∥	34

Polyimide layers have been claimed to align MBBA homogeneously[27] but our investigation proved that the alignment is generally parallel but not uniform. The alignment properties of most polymers have been evaluated, and Table II summarizes our results for cast films, together with the available published data. A wide variety of methods[34] has been used to form the polymer layer which is preferably thin in order to avoid an excessive potential drop in the dielectric layer. The film may be transferred to the surface from a liquid, while polymer casting and thermal or plasma polymerization of the monomer have also been used. The most common method is to form the polymer from partially polymerized solution by dipping or spin coating followed by curing. That the condition of film formation determines the final result may be indicated by the case of polytetrafluoroethylene (PTFE) films. As a result of an experiment with a series of photopolymerized 1000 Å PTFE films we observed that some films gave a homeotropic alignment while others did not. An attempt to determine the critical surface tension of these films proved that a continuous variation of the contact angle of liquids of different surface energy could not be obtained on those films which did not align LCs. It was also observed that films obtained from fluorinated polymer suspensions did not give homeotropic alignment of ester or biphenyl mixtures. It has been reported that MBBA does not align on PTFE films transferred by sliding contact on to glass substrates,[38] while sputtered PTFE films align most LCs, including MBBA.[34] Such a discrepancy is evidently related to the state of the surface of the deposited film.

Smooth, uniform polymer layers of PTFE and silicones induce homeotropic alignment of most commercial LCs with the exception of phenylcyclohexane (Merck Zli 1132) and tolan[34] mixtures. Alignment of these mixtures may be obtained by plasma polymerization of fluorinated alkene monomers[25] or perfluorocycloalkanes[31] and by films deposited from silicone solutions (see also paragraph 4). These homeotropically aligning plastic films excepted, other polymers, including plasma deposited films, do not give an uniform parallel alignment and a further rubbing is needed to provide uniformity.

Polymer coatings do not sustain high temperatures and displays employing such coatings must be sealed with an adhesive which is compatible with the polymer layers. This calls for a careful choice of adhesive in the case of silicones. Fluorinated polymers deposited by plasma polymerization of perfluorocycloalkanes,[31] as well as polyimide layers[30] are reported to be compatible with a glass frit sealing.

> In general, smooth layers of glasses, oxides or polymers orient the nematic director parallel to the substrate but do not induce uniform, reproducible LC alignment.

TABLE II (*continued*)

10

Polymer	Commercial name	Source	10^{-3} J m^{-2}	Mode of coating	Surface state	Liquid crystals	Alignment	Ref.
Polyparaxylylene								
p.(p. xylylene)	Parylene	(Union Carbide) (Backelite)	···	Vapor polym.	Rubbed	DIBAB	∥	29
		(BXC)	···	Vapor polym.	Rubbed	5CB	∥	34
Polyesters, polyurethanes								
p. esters	Lumi rror	Toray	40–43	Polym. sol.	Rubbed	Schiff base mixt.	∥	
p. esters	Mylar A. B. C	Dupont	40–43	Thick film	Natural	MBBA/TN200/ TN103, E7 azoxy ent.	×	20
p. esters	Mylar A. B. C	Dupont	40–43	Thick film	Rubbed	MBBA/TN200/ TN103, E7 azoxy ent.	∥	20
p. esters	Melinex	ICI	40–43	Thick film	Natural	MBBA/TN200/ TN103, E7 azoxy ent.	×	20
p. esters			40–43	Thick film	Rubbed	MBBA/TN200/ TN103, E7 azoxy ent.	∥	20
p. esters	Hostaphan	Kalle	40–43	Thick film	Natural	MBBA/TN200/ TN103, E7 azoxy ent.	×	20
p. esters	Hostaphan	Kalle	40–43	Thick film	Rubbed	MBBA/TN200/ TN103, E7 azoxy ent.	∥	20
p. urethane	V. Chroma	Daï Nippon Toryo		Polym. sol.	Rubbed	Schiff base mixt.	∥	36
Polyamides								
p. amide	Capran	All Chem.	33–42	Thick film	Natural	TN200, TN103, E7	×	20
					Rubbed	TN200, TN103, E7	∥	20
p. amide	Versamid	Gen. Mills	33–42	Sol. in LC	Natural	MBBA	⊥	56
p. methylamide (Nylon 6)	Sumitherm	Sumi Denks	···	Polym. sol.	Natural	Schiff bases	×	36
Polyimides								
p. imide	Nolimid	Rhône Poulenc	···	From monomer sol.	Rubbed	TN200, TN103, TN104, E7	∥	20
p. imide	Nolimid	Rhône Poulenc	···	From monomer sol.	Rubbed	E8, ZLi1132	∥	20
p. imide	Nolimid	Rhône Poulenc	···	From monomer sol.	?	MBBA	∥	27
p. imide	Nolimid	Rhône Poulenc	···	From monomer sol.	Rubbed	Schiff bases, CB, Esters azoxys, azo	∥	30,31
p. imide	Kapton	Dupont	···	Thick film	Natural	TN200, TN103, TN404, E7, E8	× ×	20 20
p. imide	Kapton	Dupont	···	Thick film	Rubbed	TN200, TN103, TN404, E7, E8	∥	20
Polysulfone								
p. sulfone	S 179	Appl. Sc. Lab	41	Polym. sol.	Natural	TN103, E7, azoxy	×	20
					Rubbed	n. esters mixture	∥	20
Polyheterocycles								
p. quinoxaline	···	Monomer	···	Polym. sol.	Rubbed	p. nematic mixt.	∥	28
p. benzthiazole	···	Monomer	···	Polym. sol.	Rubbed	p. nematic mixt.	∥	28
p. benzoxazole	···	Monomer	···	Polym. sol.	Rubbed	p. nematic mixt.	∥	28
Cellulose derivatives								
Methyl cellulose 65SH4000	···	Shinetsu Kagaku	35–42	Polym. sol.	Rubbed	Schiff base mixt.	I	36
Cellulose acetate	···	Ceta SA	39	Thick film	Natural	MBBA/TN103/ E7/azoxys	×	20
Cellulose acetate		Ceta SA	39	Thick film	Rubbed	MBBA/TN103/ E7/azoxys	∥	20
Cellulose acetate	LT105	Daicel	39	Polym. sol.	Rubbed	Schiff base mixt.	∥	36
Cellulose triacetate and various esters	LT105	Daicel	39	Polym. sol.	Rubbed	Schiff base mixt.	∥	36
Nitrocellulose	H1G40	Asai Kasei	34–42	Polym. sol.	Rubbed	Schiff base mixt.	∥	36
Nitrocellulose	Celluloid	···	34–42	Thick film	Natural	TN200/TN103/ E7/azoxys	×	20
Nitrocellulose	Celluloid	···	34–42	Thick film	Rubbed	TN200/TN103/ E7/azoxys	∥	20
Polysilanes								
p.(glycidopropyl-trimethoxysilane)	···	···	41 (34)	Dipping in monomes sol.	Nat ?	MBBA, esters, tolans, CB	∥	34
p. hexamethylsiloxane	···	···	24 (34)	Plasma polym.	Natural	MBBA, esters, tolans, CB	⊥	34
Silicone rubber	KE45	Shinetsa Kagaku	22–24	Polym. sol.	Natural	Schiff base mixt.	⊥	36
Silicone rubber	CAF RTV	Rhône Poulenc	22–24	Polym. sol.	Natural	TN200/103-E7, azoxys	⊥	20

TABLE II (continued)

Polymer	Commercial name	Source	10^{-3} J m^{-2}	Mode of coating	Surface state	Liquid crystals	Alignment	Ref.
Silicone rubber	Elcon III	Chemie Moudon	22-24	Polym. sol.	Natural	TN200/103-E7. azoxys	⊥	20
p. ester silicone	...	Frabera	22-24	Thick film	Natural	TN200/103-E7. azoxys	⊥	20
p. methylphenylsiloxane	...	...	22-24	Dipping	Natural	MBBA/EBBA azoxys	⊥	16
p. methyl p. dimethylsiloxane	...	...	22-24	Dipping	Natural	MBBA/EBBA	⊥	16
p. methylsiloxane mixt.	...	...	22-24	Polym. sol.	Natural	p. S. Bmûl	⊥	98
p. methyl, phenyl (45%) siloxane	Si 996	Rhône Poulenc	...	Sol.	Natural	E7	⊥	20
p. methyl, phenyl (45%) siloxane	Si 996	Rhône Poulenc	...	Sol.	Natural	103	X	20
p. methyl, phenyl (45%) siloxane	Si 996	Rhône Poulenc	...	Sol.	Natural	1132	X	20
Fluorinated polymers								
p. tetrafluoroethylene	Teflon	Dupont	16-22	Sputtering	Natural	MBBA, esters.	⊥	34
p. tetrafluoroethylene	...	...	22 (34)	Plasma polym.	Natural	CB tolans	‖	25a
p. tetrafluoroethylene	...	...	16 (38)	Sliding contact	Natural	MBBA, Chlorosilbene.	X	38
p. tetrafluoroethylene	...	...	not meas-urable	Photo polym.	Natural	CB, TN103 azoxys Chlorosilbene.	X	20
p. fluoropropyl Co tetrafluoroethylene FEP	...	Dupont	16-16.5	Thick film			X	20
p. vinylidene fluoride	Tedlar	Dupont	32.3	Thick film	Rubbed		‖	20
p. 1,3-dimethylcyclohexane	...	...	18 (32)	Plasma polym.	Natural	Schiff base mixt.	⊥	32
p. perfluorocyclohexene	...	...	22-24 (32)	Plasma poly.m.	Natural	Schiff base mixt.	⊥	32
p. perfluoro	...	...	20-22 (32)	Plasma polym.	Natural	Schiff base mixt.	⊥	32
p. acetylene Co perfluoro-1,3-dimethylcyclohexane	...	...	18-31		Natural	Schiff base mixt.	⊥-‖	37
Others								
Urea-formaldehyde resins/viloid	...	Mitsubishi Toaku	61	Polym. sol.	Rubbed	Schiff base mixt.	‖	36
Epoxies	ER 664	Asahi Kasei	35	Polym. sol.	Natural	Schiff base mixt.	‖	36
Phenolic resins	Beckosol	Dai Nippon	52	Polym. sol.	Natural	Schiff base mixt.	‖	36
Casein	...	...	43	...	Natural	Schiff base mixt.	‖	35
Ionomere	Surlyn Na	Dupont	...	Thick film	Natural	103.E7.	X	20
	Surlyn Na	Dupont	...	Thick film	Rubbed	103.E7.	‖	20
Coumarone–Indene	...	...	—	...	Rubbed	...	‖	35

ᵃ Critical surface tension from Polymer Handbook, 2nd ed., edited by J. Brandrup and E. H. Immergut, (Wiley, New York, 1975), except as otherwise indicated.

⊥ = homeotropic alignment (perpendicular to glass surface); ‖ = alignment, uniform, parallel to glass surface; ● = molecular alignment too difficult to distinguish between perpendicular and parallel alignments and to obtain consistent experimental results; ‖/⊥ = molecular alignment changed near the phase transition temperature from the parallel alignment at lower temperatures to the perpendicular alignment at higher temperatures; X = parallel nonuniform.

I.2 Alignment on grooved surfaces

Rubbing, tangential evaporation or shallow angle ion beam etching (SAIBE) produce a wavy surface. It has long been acknowledged that the rubbing of a glass plate induces uniform alignment of LCs,[39,40] with the nematic director nearly parallel to the substrate surface.[41] For some time it was considered that the material used for rubbing determined the efficiency of the process.† It is now clear, however, that, as proposed many years ago,[39] any rubbing material, e.g., paper, tissues, brushes and polishing powders, gives good results. Some LCs align more easily than others and reproducibility is not very good on substrates that are simply rubbed. The use of polishing powder, such as diamond paste, improves the alignment and is a requisite for hard layers of silica or fluoride.

Glass has a surface layer extending one micron in depth which has higher entropy than the bulk[42] and may be easily deformed by rubbing, producing a wavy surface. Because of its higher energy this surface layer melts 125°C below the softening point of the glass[42] (i.e., around 475°C for soda lime glass) and, therefore, the effects of rubbing disappear above this temperature. Glass frit sealed cells, therefore, require the use of layers of high melting point compounds. SiO_2 deposited by sputtering, CVD or an electron gun, as well as MgF_2.[15,20] $BaTiO_4$, TiO_2,[22] Cs_2O, Y_2O_3, BN,[19] CeO[19] or Si_3N_4[18] layers give, after rubbing with diamond paste or cerium oxide powder,[43,20] good, homogeneous aligning layers but the results are very sensitive to further processing. It is likely that these hard materials are difficult to groove sufficiently.

Oxides,[17] fluorides and metal layers evaporated obliquely to a substrate generally align the LC molecules parallel to, or at a slight angle from, the surface[44] but tangentially evaporated calcium fluoride is reported to align the molecules nearly perpendicular[12] although we could not reproduce this result. Slant evaporation of a metal and subsequent thermal oxidation[21] or shallow angle ion beam etching (SAIBE)[45a] produce the same results. Obliquely evaporated SiO_x and MgF_2 layers give reproducible results and this method is widely used for the fabrication of small displays; it is further compatible with any type of sealing.

When high temperature resistance is not required, as in experimental cells or plastic sealed displays, it is advantageous to coat the electrodes with a soft polymeric layer which is rubbed afterwards. Any polymer is suitable, pro-

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† Alignment of LCs by rubbed surfaces is sometimes wrongly attributed to J. F. Dreyer who omitted, in his paper "Orientation of the surface of glass" [Glass, Ind. 29, 197 (1948)], to quote the work of Zocher and Coper (Ref. 39). This point has been cleared up in a letter to the editor by C. D. West [Glass, Ind. 30, 272 (1949)], which provides an English translation of the main paragraph of Ref. 39. P. Chatelain,[40] who studied in detail LC alignment by rubbed surfaces, also ignored this work which clearly established the influence of rubbed glass surfaces on the orientation of PAA (which was used to prove the glass surface anisotropy) and that it was a property of the clean surface.

vided that it is possible to deposit it as a thin film (Table II) and most LCs will align homogeneously. Rubbed polyvinyl alcohol or polyvinyl butyraldehyde have been proposed as a method of forming an internal polarizer and an aligning layer simultaneously,[33] but the polarizing effect is weak. The quality of the alignment depends on the polymer layer thickness and the substrate uniformity. It is often advantageous to provide the electrodes with an intermediate layer that promotes adhesion and uniformity. As previously described, a wide variety of methods has been used to form films on a glass substrate. The rubbing of substrates on which a polymer powder was spread, or rubbing with a piece of polymer, have also been described as producing good aligning layers.[46] Although the surface deformation of glasses and polymers has not been clearly shown, the grooves produced by rubbing with a polishing paste[43,47] and the striated nature of tangentially evaporated layers[48-53] has been shown by photomicrographs. A grating made of a photoresist layer[47,54] or of SiO_2[51] induces homogeneous alignement of a LC.[47,50] Many surfaces tend to align LC's parallel and striations on these surfaces provide uniformity, which has led to the claim that any striated surface, whatever the substrate and the method used to produce them,[55] induces homogeneous alignment. In fact homeotropic aligning layers, e.g., evaporated CaF_2, show at most a leaning of the molecular axis when striations are induced by oblique evaporation, and polymethylsiloxane still promotes an homeotropic alignment after it has been rubbed (see Figure 9).

One point which is not clear is the surface nature of evaporated inorganic layers which are sometimes found to induce homeotropic alignment (not in a reproducible manner) but, once rubbed, promote a homogeneous alignment.

I.3 Alignment by surface active agents

It has long been observed[56] that surface active agents promote LC alignment. They may be either dissolved in a LC, or deposited on the cell walls. Small amount of surfactants may be dissolved in LCs conveniently through a common solvent which is evaporated afterwards. Spontaneous homeotropic alignment of the mixtures is observed on glass or oxide surfaces. Most surfactants have been described as effective (Table III) and examples are given for negative LC mixtures. These observations have been hastily extended to "liquid crystals", in general. As surfactant induced alignment is complex depending on the substrate, mode of application, LC composition (see § II.1.8), the use of these data needs critical evaluation.[57,65] For displays operating in the field effect mode, the increase in conductivity due to an ionic dopant is a disadvantage and, therefore, nonionic compounds are preferred. Cationic surfactants, which are long chain substituted ammonium salts, are very effective in promoting homeotropic alignment of negative[58-60] and positive[20,17] LCs although they increase the LC conductivity. Figures obtained for various con-

TABLE III

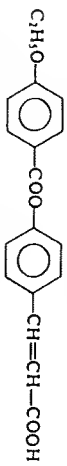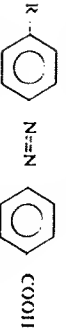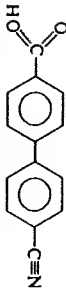Surfactants agents reported to induce homeotropic alignment of nematic LCs

Surfactants	Liquid crystal	Ref.
1. ANIONIC		
1.1. ACYCLIC CARBOXYLIC ACIDS: R-COOH		
R = CₙH₂ₙ₊₁ $n > 10$	MBBA	5
$n = 8, 11, 19$	n-Schiff base mixt.	61
	n-Ester mixt.	60
R = C₈H₁₇CH=CH-(CH₂)₇ $n = 18$ (stearic acid)	MBBA	60
(oleic acid)	MBBA	
R = CₙF₂ₙ₊₁ $n = 18$	Esters	3
R = CₙH₂ₙ₊₁ R-(COOH)₂ $n = 18$ (octadecylmalonic acid)		64
1.2. AROMATIC ACIDS: R-⟨ring⟩-COOH		
R = 4NH₂, 4 OH; 3 OH	n-Schiff base mixt.	61
R = CₙH₂ₙ₊₁O	n-Ester mixt.	62
$n = 9, 10, 12, 14, 16, 18$	n-Azoxy mixt.	66
R = CₙH₂ₙ₊₁ $n = 8$		62
R = CₙH₂ₙ₊₁O $n = 6, 12$		
R = CₙH₂ₙ₊₁-COO $n = 3, 17$		
R-⟨ring⟩-CH₂COOH		
R = 4NH₂, 4 OH; 3 OH	n-Schiff base mixt.	61
	n-Ester mixt.	
	n-Azoxy mixt.	
R-⟨ring⟩-(CH₂)₂-COOH		
R = 4NH₂, 4 OH; 2-5 OH	n-Azoxy mixt.	61
R-⟨ring⟩-CH=CH-COOH		
R = 4NH₂, 4 OH; 3-4 OH		
R = CₙH₂ₙ₊₁O $n = 10, 12, 18$	n-Azoxy mixt.	62
R = CₙH₂ₙ₊₁-COO $n = 1, 12, 18$		
R₁ = C₆H₁₃O R₂ = Cl		
R₁ = C₁₄H₂₉O R₂ = Cl	n-Ester mixt.	56
1.3. CARBOXYLIC ACID WITH LC STRUCTURE		
1.3.1. Derivatives of Schiff's base		
RₙCH=N-⟨ring⟩-CH=N-⟨ring⟩-R' COOH		

TABLE III (continued)

Surfactants	Liquid crystal	Ref.
R' = H, Rₙ = 4 OH. 3 OH. 2 NO₂-3 OH. 3-4 OH. 2-4 OH. 2-4-6 OH	n-Schiff base eut. mixt.	61. 62
	n-Esters eut. mixt.	
	n-Azoxy eut. mixt.	
	n-Azo eut. mixt.	
Rₙ = CₙH₂ₙ₊₁O $n = 1, 7, 13$		
Rₙ = CₙH₂ₙ₊₁ $n = 1, 4, 7, 13$		
R' = OH Rₙ = CₙH₂ₙ₊₁O $n = 0, 1, 3, 7, 13$		
Rₙ-⟨ring⟩-CH=N-⟨ring⟩-CH₂COOH	As above	61
Rₙ = 4 OH, 3 OH, 3-4 OH		
Rₙ = CₙH₂ₙ₊₁O $n = 1, 3, 4, 15$		
Rₙ = CₙH₂ₙ $n = 1, 4, 7, 13$		
Rₙ-⟨ring⟩-CH=N-⟨ring⟩-(CH₂)₂COOH		
R = 4 OH		
R = CₙH₂ₙ₊₁O $n = 1, 4, 7, 13$		
R = CₙH₂ₙ₊₁ $n = 1, 4, 7, 11$		
R-⟨ring⟩-CH=N-⟨ring⟩-CH=CH-COOH	n-Ester mixt.	56
R = C₇H₁₇O		
R-⟨ring⟩-CH=C-COOH with CH₃	n-Ester mixt.	56
R = CH₃O R = C₂H₅O (slow)		
1.3.2. Derivatives of LC azoxy structure		
Rₙ-⟨ring⟩-N=N(O)-⟨ring⟩-COOH	n-Azoxy eut. mixt.	62
R = CₙH₂ₙ₊₁O $n = 1, 2, 4, 6, 12, 18$		
R = CₙH₂ₙ₊₁COO $n = 3, n = 15$		
Rₙ = CₙH₂ₙ₊₁ $n = 14$		
R-⟨ring⟩-N=N(O)-⟨ring⟩-C=C-COOH	n-Azoxy eut. mixt.	62
R = CₙH₂ₙ₊₁O $n = 2, 4$		
1.3.3. Derivatives of LCs with ester structure		
R-⟨ring⟩-COO-⟨ring⟩-COOH	n-Azoxy mixt.	62
	n-Ester eut. mixt.	

TABLE III (continued)

Surfactants	Liquid crystal	Ref.
C₂H₅O—[structure]—COO—[structure]—CH=CH—COOH R = CₙH₂ₙ₊₁O　　n = 10, 14 R = CₙH₂ₙ₊₁　　n = 4, 8, 18 R = CₙH₂ₙ₊₁COO　　n = 3, 15, 17	n-Azoxy eut. mixt.	62
1.3.4. Derivatives of LCs stilben structure R—[benzene]—CH=CH—[benzene]—COOH R = CₙH₂ₙ₊₁O　　n = 8, 18 R = CₙH₂ₙ₊₁COO　　n = 6, 9	n-Azoxy mixt. Chloro stilben mixt.	62
1.3.5. Derivatives of LCs azo structure R—[benzene]—N=N—[benzene]—COOH R = CₙH₂ₙ₊₁O　　n = 1, 6, 12, 18 R = CₙH₂ₙ₊₁　　n = 6, 10, 14 R = CₙH₂ₙ₊₁COO　　n = 3, 7, 15	n-Azo eut. mixt.	62
1.3.6. Derivatives of cyanobiphenyls HO—O=C—[benzene]—[benzene]—C≡N	E7	45c
1.4. ANIONIC SURFACE ACTIVE AGENTS Cobalt, zinc naphthenate	MBBA	58
Sulfated alcohols	MBBA	58
Sulfated ethers	MBBA	58
2. CATIONIC **2.1. ALKYL AMMONIUM SALTS**　CₙH₂ₙ₊₁—N⁺(R)₃ X⁻ **2.1.1. X⁻ = halogen** n > 10	MBBA	75
n = 16 (Cetyl trimethyl ammonium bromide)	MBBA	58,57
n = 16 (Cetyl trimethyl ammonium bromide)	n-Ester mixt.	58,59
n = 16 (Cetyl trimethyl ammonium bromide)	PAA	58
CₙF₁₇SO₂NH(CH₂)₃N⁺(CH₃)₃	MBBA-157, TN103, ZLi1132	75-20
2.1.2. X⁻ = benzoate	n-Schiff base mixt.	70 59
[CH₃/C₂H₅/CH₃] C₆H₁₃—N⁺—C₂H₅ ⊖OOC—[benzene]—OC₆H₁₃		62
C₆H₅—N⁺—(CH₃)₃ ⊖OOC—[benzene]—C₂H₅	n-Schiff base mixt.	70

TABLE III (continued)
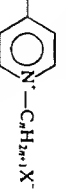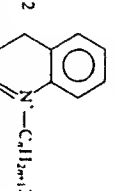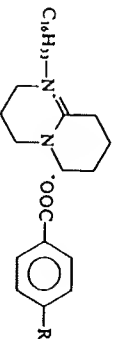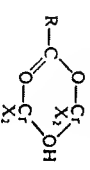
Surfactants	Liquid crystal	Ref.
2.1.3. X⁻ = teraphenyl borate (C₁₈H₃₇)₂N⁺(CH₃)₂—(C₆H₅)₄B⁻	n-Schiff base mixt.	69
2.2. ALKYLPYRIDINIUM SALT [pyridine]—N⁺—CₙH₂ₙ₊₁ X⁻ n = 16, 12　(X⁻ = Br⁻)	n-Schiff base mixt.	59
n = 16　(X⁻ = (C₆H₅)₄B⁻)	n-Ester mixt.	59
2.3. ALKYLISOQUINOLINIUM SALTS n = 12	PAA	54
2.4. 7-ALKYL-1,8-DIAZABICYCLO[5.4.0]UNDECENAMMONIUM C₁₆H₃₃—N⁺=N⁻ ⁻OOC—[benzene]—R'	n-Schiff base mixt.	70
R' = NH₂, NO₂, Cl, H, CH₃, C₃H₇, C₄H₉, C₆H₅	n-Azoxy mixt. n-Ester mixt.	59 59
2.5. CARBOXYLATOCHROMIUM COMPLEXES R—C(O)—O—Cr(X₂)—O—Cr(X₂)—OH	n-Schiff base mixt. CB p-Schiff base	73
3. NONIONIC **3.1. ALIPHATICS ESTERS, NITRILES, UREA, AMINES OR ALCOHOL** R—COO—CₙH₂ₙ₊₁　R = CH₃ n = 8, 18	n-Schiff base mixt.	74
CₙH₂ₙ₊₁COO R　R = CH₃ n = 11	n-Schiff base mixt.	61
CₙH₂ₙ₊₁—CN　R = 6 n = 7	MBBA	60
C₁₈H₃₇—HN—CO—NH₂ n = 16	MBBA	66
CₙH₂ₙ₊₁—NH₂ n > 12	MBBA	5
n = 16	MBBA	75
n = 18	MBBA	60

TABLE III (continued)

Surfactants	Liquid crystal	Ref.
$C_nF_{2n+1}CF=CF(CH_2)_2NH(CH_2)_2N(CH_3)_2$ $n = 6$	MBBA/EBBA	92
C_nH_{2n+1}—OH (amine catal.) $n = 12, 14, 16, 18$	n-Ester eut. mixt. / MBBA	76 / 66
$C_nF_{2n+1}(CH_2)_nOH$ $n = 7, m = 3$	MBBA/EBBA	92

3.2. AROMATIC ACID ESTERS

H_2N—⬡—$(CH_2)_m$—$COOC_nH_{2n+1}$ $n = 6$ to 16, $m = 0, 1, 2$	n-Schiff base mixt.	63
X_n—⬡—COO—C_nH_{2n+1} $n = 4$ to 12, $X_n = 4$ OH; $n = 2$ to 18, $X_n = 1, 2, 6$ OH	n-Schiff base mixt.	63 / 61

3.3. PHENOLS, AROMATIC AMINES

2,6 Di-t-butyl-4-muthylphenol	MBBA	71
Hydroquinone	MBBA	71
4-t-butylpyrocatechin	MBBA	71
2-t-butylhydroxyanisole	MBBA	71
Nisopropyl-N-phenyl p. penylenediamine	MBBA	71
Phenyl-β-naphthylamine	MBBA	71
p-hydroxyphenyl-β-naphthylamine	MBBA	71

3.4. NONIONIC SURFACTANTS

Epoxy resins (low molecular weight)	MBBA	67
Polyamid resins (low molecular weight)	MBBA	56
Alkyl phenyl ethers	MBBA	67
Polyoxyethylated glycols	MBBA	67
Fluoro polymers	MBBA	67

4. AMPHOLYTICS

Lecithin egg Lecithin	MBBA	79-6
egg Lecithin	E7, E8, TN103, TN404, 1132	20
α Lecithin CH_2—CH—$CH_2O'PO,\ominus(CH_2)_2N^+(CH_3)_3$ R_1 R_2	PCH, Schiff bases, azoxy, esters	65

centrations of cetyl ammonium bromide in a positive ester mixture ROTN 103 are given in Table IV.

The use of these agents has, therefore, been proposed for dynamic scattering mode displays.[46,59] Alignment of positive LCs is also observed with these compounds. Alkylvinyl pyridinium halides provide stronger orientation than ammonium derivatives, being able to align even smectic phases. In fact most

TABLE IV

Alignment and conductivity (σ) of p. ester mixture TN103, with added CTAB

% CTAB	0	0.01	0.1	0.25	0.5	1
σ	1.8×10^{-10}	2×10^{-10}	10^{-9}	1.7×10^{-9}	2.9×10^{-9}	7.4×10^{-8}
LC alignment	‖	‖	=	●	⊥	⊥⊥

compounds of this type, dissolved in LCs, favor homeotropic alignment of the LC. Fatty nitriles, amines,[60] acids[6,61] and esters[61] align MBBA. The effect of nitriles and esters is weak, depends on the substrate, and fails to align biphenyl and ester mixtures. Substituted benzoic acid[61,62], its ester, phenols[15,52,54] and octadecyl malonic acid[64] are also effective, but branched isopalmitic acid does not align a LC.[65] Derivatives of benzoic acids which possess a liquid crystal structure have been thoroughly investigated[61,62] and a critical study[57] has assessed the more effective dopants. Such compounds, being frequently present as impurities or decomposition products in a LC, cause wrong correlations between LC structures and surface treatments. Their effect appears stronger when they are formed in the cell by LC degradation than when added to the LC. Effective concentrations of additives to the LC are in the range 0.5% to 2%. At smaller concentrations, the alignment presents defects, and higher concentrations lower the nematic to isotropic transition temperature significantly. The main drawback of this method of alignment is that on filling a cell provided with only one fill port, as preferred in industry, the additives absorb strongly in the neighborhood of the aperture and the liquid crystal at the end of the cell contains a lower concentration of additive, producing defects and a conductivity gradient across the cell. Attempts have been made to treat the cell walls before filling. Most of the surfactants described above for doping LC mixtures are effective, as the dissolved surfactant aligns the LC through absorption on the cell walls.

The orientation of the LC depends on its molecular structure: while most LCs are homeotropically aligned by adsorbed lecithin, azoxy derivatives and 4-methoxypropylcarboxybenzylidene aniline are not aligned.[65] The packing density of the adsorbed amphiphilic layer also plays a role. While homeotropic alignment of MBBA on glasses covered with hexadecyl(=cetyl)trimethyl ammonium bromide(CTAB) occurs at high coverage,[8] lecithin's orienting power decreases with increasing packing density.[65] Fatty amines[5] and alkyl substituted ammonium derivative[66] chains with a carbon content over 10 promote homeotropic alignment, while shorter chains orient the nematic director at an angle from the surface, smaller angles being observed for shorter chains. Heating destroys the aligning layer and cells provided with one fill port must be treated with a solution of the surfactant in a volatile solvent, rinsed,

dried and filled. Although often used in experimental work with lecithin in ether, or CTAB in alcohol, this method has not found industrial acceptance.

These methods give good results on many substrates except plastic coatings but long term stability is not obtained as the absorbed layer slowly dissolves in the LC.

Attempts have been made to bind the surface active molecule covalently to the surface. Baking octadecyltrimethyl ammonium tetraphenyl boride absorbed on cell walls from a solution has been claimed[69] to improve the alignment of the negative Schiff's bases. Reaction of fatty alcohols with silica covered electrodes catalyzed by amines[45b] seems to depend on the quality of the silica layers as we did not obtain reproducible results on silica layers deposited by CVD or solutions of organosilicon compounds. Tributyltin oxide[71] or chloride[72] dissolved in the LC produces homeotropic alignment, probably due to reactions with the electrode surface. The best results are obtained with carboxylatochromium complexes[73] or silanes which are substituted with one long chain polar group,[77] e.g., N-octadecyl-N,N-dimethyl-3-aminopropyltrimethoxysilyl chloride. We have checked that the aligning power is strong for most positive nematic mixtures and effective on rubbed layers, providing a way of realizing both homogeneous and homeotropic domains in the same cell by selective treatment of the walls. Nevertheless, these compounds, being ionic, increase slightly the LC conductivity even with thoroughly cleaned surfaces. Surfactants may also be included in a polymer layer, where they act as plasticizers: long term stability has not yet been evaluated. Long chain polar compounds generally induce homeotropic alignment of most practical LC mixtures. Few additives, however, promote planar alignment. Dicarboxylic acids added to LC mixtures are claimed to impart horizontal orientation.[76] Also, surfaces treated with N-methyl-3-aminopropyltrimethoxysilane align MBBA and N-p-(cyanobenzylidene)-p-N-octylaniline homogeneously after rubbing,[77] but we found that the very similar N-ethyl-3-aminopropyltrimethoxysilane aligns E7 and ROTN 103 homeotropically. Chromium complexes of dicarboxylic acids align negative LCs homogeneously, whereas homeotropic alignment is observed for positive mixtures.[78] Diazapolyoxycycloalkanes (crown ethers) improve homogeneous alignment on most oxides.[80] A large increase in LC conductivity, however, is observed when these compounds are used.

It is interesting to note that reacting tin oxide layers with long chain alcohols ($C_nH_{2n+1}OH$, $n = 1$ to 20), triethanolamine, phenols, cyclohexanol, phenyl acetic acid or valeric acid under pressure promotes homogeneous alignment of LCs as opposed to previous observations. An example is given for tin oxide treated either with n-decanol or cinnamic alcohol on an alkyloxyphenylpyrimidine mixture.[81]

agents and sometimes considered as polymer forming compounds. As they are of interest for LC alignment they justify a special paragraph.

I.4 Alignment by silane treated surfaces

Alkoxys and chlorosilanes interact strongly with glass surfaces. The proposed mechanisms are either reaction with surface silanol groups, or hydrolysis of the silane to a silanol which will further condense into a linear polysiloxane layer (Figure 1). Thus silanes are sometimes considered as surface active agents and sometimes considered as polymer forming compounds. As they are of interest for LC alignment they justify a special paragraph.

Surface treatments with silanes have been effected by dipping during 5 to 1 hr., (generally 5 min) in 1%–5% solution of the silane in water, toluene, dilute acetic in water, DMF or acetone. Water solutions are stable for only a few hours (except aminosilanes). After rinsing with the solvent used to dissolve the silanes.[72a] In the case of quaternary ammonium sylil compounds these methods gave poor results with most LCs and dipping in hot (75°C) solutions[83] improved the efficiency of the treatment. Silanation also occurs if the substrate is exposed to silane vapor, for low boiling point compounds, or treated in a refluxed solution of silane in toluene, for others. We have often observed that depositing a drop of pure silane on a spinning substrate often gave better results than dipping in silane solutions. Hydrolysis of the surface before coating is sometimes recommended. An evaluation of silane alignment efficiency for the alignment of the positive ester mixture ROTN 103, and the biphenyl mixture E7, is presented in Table V together with some published results. It can be seen that the effect of the silane layer depends on the mode of deposition and the nature of the LC. Among the different silanes which have been tried, monodimethyldichlorosilane shows a strong effect, unlike the similar ethyl substituted derivatives, and methyltrichlorosilane or trimethylchlorosilane. Stearyltrichlorosilane has been reported to align Schiff's bases and biphenyls homeotropically.[87] Those silanes which do not align homeotropically can only be persuaded to align a wide range of LCs uniformly and parallel to the substrate, after rubbing, as has already been noted. It seems that most silanes influence the LC alignment by the in situ formation of a polysiloxane surface layer. Deposition of silicones which are formed by bulk polymerization of silanes shows that only methylpolysiloxane (and for some LCs, methylphenylsiloxane) aligns LCs homeotropically, while the remainder promote a planar alignment, contrary to certain reported observations.[86] In fact, silanes may be used in two ways: either to form a polysiloxane layer or to bind a long chain to the substrate, as with stearylsilane or dodecylammonium compounds. A substrate may alter the film properties and it is advantageous to form an initial surface layer by decomposition of an organometallic compound before silane treatment. Silylated surfaces degrade upon heating and

TABLE V (*continued*)

26

J. COGNARD

ALIGNMENT OF LIQUID CRYSTALS

27

Silane	Supplier	10^{-3} J m^{-2}	Liquid crystal	Treatment	Time	Temp. °C	Ref.	Align.
			C$_{10}$H$_{21}$O–ϕ–CH=N–ϕ–C≡N				87	⊥
			C$_6$H$_{11}$–ϕ–ϕ–C≡N				87	⊥
			C$_6$H$_{13}$–ϕ–ϕ–C≡N				87	●
			C$_7$H$_{15}$–ϕ–ϕ–C≡N				87	●
			CH$_3$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	⊥
			C$_2$H$_5$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	⊥
			C$_3$H$_7$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	⊥
			C$_4$H$_9$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	⊥
			CH$_3$O–ϕ–N=N–ϕ–OCH$_3$ O				87	‖
			C$_2$H$_5$O–ϕ–N=N–ϕ–OC$_2$H$_6$ O				87	‖/⊥
			C$_5$H$_{11}$O–ϕ–N=N–ϕ–OC$_5$H$_{11}$ O				87	⊥
			CH$_3$O–ϕ–CH=N–ϕ–OO–C–CH$_3$				87	‖/⊥
			C$_2$H$_5$O–ϕ–CH=N–ϕ–OO–C–CH$_3$				87	‖/⊥
			CH$_3$O–ϕ–CH=N–ϕ–OO–C–C$_2$H$_5$				87	‖/⊥
			C$_2$H$_4$O–ϕ–CH=N–ϕ–OO–C–C$_3$H$_6$			⊥	87	‖/⊥
Diphenyl			CH$_3$O–ϕ–CH=N–ϕ≡C–N	5% in toluene	10 min	room temp.	87	‖
			C$_2$H$_5$O–ϕ–CH=N–ϕ≡C–N				87	‖
			C$_4$H$_9$O–ϕ–CH=N–ϕ≡C–N				87	‖
			C$_6$H$_{11}$O–ϕ–CH=N–ϕ≡C–N				87	‖
			C$_8$H$_{17}$O–ϕ–CH=N–ϕ≡C–N				87	‖
			C$_{10}$H$_{21}$O–ϕ–CH=N–ϕ≡C–N				87	‖
			C$_5$H$_{11}$–ϕ–ϕ–C≡N				87	‖
			C$_6$H$_{13}$–ϕ–ϕ–C≡N				87	‖
			C$_6$H$_{13}$–ϕ–ϕ·C≡N				20	●
			C$_7$H$_{15}$–ϕ–ϕ–C≡N				87	‖
			CH$_3$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	‖
			C$_2$H$_5$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	h
			C$_3$H$_7$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	‖
			C$_4$H$_9$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	‖
			CH$_3$O–ϕ–N=N–ϕ–OCH$_3$ O				87	‖
			C$_2$H$_6$O–ϕ–N=N–ϕ–OC$_2$H$_6$ O				87	‖
			C$_5$H$_{11}$O–ϕ–N=N–ϕ–OC$_5$H$_{11}$ O				87	⊥
			CH$_3$O–ϕ–CH=N–ϕ–OO–C–CH$_3$				87	‖/⊥
			C$_2$H$_5$O–ϕ–CH=N–ϕ–OO–C–CH$_3$				87	‖/⊥
			CH$_3$O–ϕ–CH=N–ϕ–OO–C–C$_2$H$_5$				87	●
			C$_2$H$_4$O–ϕ–CH=N–ϕ–OO–C–C$_2$H$_6$				87	‖/⊥
Trichlorosilanes								
Methyl	Fluka 69450	20.3	TN103	vapor phase	⋯	boil. 65°C	20	×
Ethyl[2]	Fluka 04970		TN103	vapor phase	1 h	boil. 98°C	20	×
Phenyl[2]	Fluka 79230		TN103	vapor phase	10 sec	boil. 98°C	20	×
Phenyl	Fluka 79230		TN103	spin coated	⋯	room temp.	20	×
Phenyl	?		CH$_3$O–ϕ–CH=N–ϕ–C–N	toluene	10 min	room temp.	87	‖
			C$_2$H$_5$O–ϕ–CH=N–ϕ–C–N				87	‖
			C$_4$H$_9$O–ϕ–CH=N–ϕ–C–N				87	‖
			C$_6$H$_{13}$O–ϕ–CH=N–ϕ–C–N				87	‖
			C$_8$H$_{17}$O–ϕ–CH=N–ϕ–C–N				87	‖
			C$_{10}$H$_{21}$O–ϕ–CH=N–ϕ–C–N				87	‖
			C$_5$H$_{11}$–ϕ–ϕ–C–N				87	‖
			C$_6$H$_{13}$–ϕ–ϕ–C–N				87	‖
			C$_7$H$_{15}$–ϕ–ϕ–C–N				87	‖
			CH$_3$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	‖/⊥
			C$_2$H$_5$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	‖/⊥
			C$_3$H$_7$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	‖
			C$_4$H$_9$O–ϕ–CH=N–ϕ–C$_4$H$_9$				87	‖
			CH$_3$O–ϕ–N=N–ϕ–OCH$_3$ O				87	‖
			C$_2$H$_6$O–ϕ–N=N–ϕ–OC$_2$H$_6$ O				87	‖/⊥
			C$_5$H$_{11}$O–ϕ–N=N–ϕ–OC$_5$H$_{11}$ O				87	⊥
			CH$_3$O–ϕ–CH=N–ϕ–OO–C–CH$_3$				87	‖/⊥
			C$_2$H$_5$O–ϕ–CH=N–ϕ–OO–C–CH$_3$				87	‖/⊥
			CH$_3$O–ϕ–CH=N–ϕ–OO–C–C$_2$H$_5$				87	●
			C$_2$H$_4$O–ϕ–CH=N–ϕ–OO–C–C$_2$H$_6$				87	●
Vinyl	Nobel		TN103	spin coated	⋯	room temp.	20	‖ on rubbed subst.
Octadecyl (or stearyl)	Fluka		E7	1% in toluene curing 130°C 20 min (fresh solutions)	1 h	room temp.	20	⊥
			1132					×
			1275					nearly ⊥
			E8	0.5% in isopropyl alcohol curing 103°C 1 h	45 min	room temp.		⊥
			404					⊥
			1132					●
			1275				20	nearly ⊥
Stearyl			CH$_3$O–ϕ–CH=N–ϕ–C–N	5% in toluene	10 min	room temp.	87	‖
			C$_2$H$_5$O–ϕ–CH=N–ϕ–C–N				87	‖
			C$_4$H$_9$O–ϕ–CH=N–ϕ–C–N				87	‖
			C$_6$H$_{13}$O–ϕ–CH=N–ϕ–C–N				87	‖

TABLE V (*continued*)

Silane	Supplier	10^{-3} J m^{-2}		Liquid crystal	Treatment	Time	Temp. °C	Ref.	Align.
	TRIAMO			1132	0.1% in toluene + sol. rinse	...	room temp.	20	‖ rubbed subst.
	TRIAMO			E7	spin coated	...	room temp.	20	●
3-Chloropropyl TMS	Dyn. Nobel CPTMO	40.5	(82)	TN103	spin coated	...	room temp.	20	‖ rubbed subst.
3-Chloropropyl TES	Dyn. Nobel CPTEO	40.5	(82)	TN103	spin coated	...	room temp.	20	‖ rubbed subst.
3-Glyceryloxypropyl TMS	Dyn. Nobel GLYMO	38–42	(82)	TN103	spin coated	...	room temp.	20	‖ rubbed subst.
3-Glycerylpropyl TMS	Shin Etsu chem	38.5	(84)	5CB MBBA PBA	1.5% in water	15 min	room temp.	84	× × ×
3-Morpholinopropyl TMS	Shin Etsu chem	42	(84)	5CB MBBA BAB	0.5% in water	15 min	room temp.	84	× × ×
3-Methacryloxypropyl TMS	Shin Etsu chem	28/31 28	(84)	5CB MBBA PBA	1% in water/ 1 methanol			84	(×) × ×
Hexamethyldisilazane	Fluka 52619			TN103	vapor phase	1 h	boil. 124°C	20	×
	Fluka 52619			TN103	spin coated	...	room temp.	20	×
Imidazolin	Dyn. Nobel IMEO			TN103	0.1% in toluene + sol. rinse	5 min	room temp.	20	‖ rubbed subst.
				404				20	‖ rubbed subst.
				E7				20	‖ rubbed subst.
				1132				20	‖ rubbed subst.
Imidazol TES	Dyn. Nobel IMEO			TN103	spin coated	...	room temp.	20	⊥ after heating
				E7	spin coated	...	room temp.	20	●
N-Phenyl-3-aminopropyl TMS	Shin Etsu chem	42	(84)	5CB	3% in 5 water/ 1 methanol	15 min	room temp.	84	nearly ×
	Shin Etsu chem	MBBA		MBBA				84	×
	Shin Etsu chem	MBBA		PBA				84	×
3-Mercaptopropyl TMS		41–42	(84)	5CB	3% in 7 water/ 1 methanol	15 min	room temp.	84	●
		41	(82)	MBBA				84	●
		41	(82)	PBA				84	×
Polyamino TMS	Toray	26	(84)	5CB	0.5% in water	15 min	room temp.	84	nearly ×
	Silicone	26	(84)	MBBA					×
		26	(84)	PBA					
N,N-Dimethyl-N-Octadecyl-3-amino-propyl TMS-chloride (DMOAP)	Dow Corning XZ-2-2300	26	(84)	MBBA	0.1% in water	5 min	room temp.	(77)	⊥
	Dow Corning XZ-2-2300	26	(84)	CBOA					⊥
	Dow Corning XZ-2-2300	26	(84)	MBBA + esters	0.5% in water	10 min	75°C		⊥
	Dow Corning XZ-2-2300	26	(84)	MBBA/EBBA					⊥
	Dow Corning XZ-2-2300	26	(84)	n-azoxy LC mixt.					⊥
DMOAP	Toray	23	(84)	5CB	water	15 min	room temp.	(84)	⊥
	Silicone			MBBA					⊥

[a] Concerning the difference between vapor and solution coated substrates, see also Ref. 88. T.E.S. = triethoxysilane; T.M.S. = trimethoxysilane. [1] γ_c from Ref. 82 except as otherwise indicated. [2] These silanes hydrolyze strongly. [3] ‖ and × are often not distinguished in the literature. In our observations only rubbed surfaces either before or after silane treatment lead to ‖ alignment for these silanes which do not induce homeotropy.

⊥ = homeotropic alignment (perpendicular to glass surface); ‖ = alignment, uniform, parallel to glass surface; ● = molecular alignment too difficult to distinguish between perpendicular and parallel alignments and to obtain consistent experimental results; ‖/⊥ = molecular alignment changed near the phase transition temperature from the parallel alignment at lower temperatures to the perpendicular alignment at higher temperatures; × = parallel nonuniform.

preclude glass frit sealing. Treatment of the assembled cell by the organic vapor could be used, but the toxicity of chlorosilanes renders the process hazardous. From Ref. 88 it seems that the surface configuration of silane films deposited from vapor and solution phases is different. Dissolution of dimethyldichlorosilane and phenyltrichlorosilane, in EBBA–MBBA has been used to promote homeotropic and homogeneous alignment, respectively, but the process is impractical as the conductivity is increased and T_c decreased.

1.5 Tilted alignment

In evaluation studies of alignment effects, classification of LC alignment into homeotropic or parallel is an oversimplification, as often, in the literature, nonhomeotropic alignment is referred to as parallel (or homogeneous). In fact, the nematic director of LC molecules generally makes an angle ϕ with the substrate surface. This "tilt angle" is required in practical twisted nematic displays in order to obtain a rotation of all the LC molecules in the same direction on the application of an electric field. The tilt supresses the formation of diffusing walls between domains with reverse twist. A careful choice of tilt on each electrode leads to a better optical appearance.

In the neighborhood of a particular surface, tilt angles are distributed around a mean value. [93] Experimental figures refer to the mean orientation of the LC director in the bulk. Literature data show some variations in tilt angle values which arise either from the precision of the measurements or from different experimental conditions. Accuracy of measurement has been discussed [94] and some indicative data are collected in Table VI. The tilt angle on SiO_x evaporated layers shows slight variations with the substrate. Layer thicknesses in the range 50–100 Å cause variations of ϕ from 16° to 22°. [95] The rate of evaporation, [96] the pressure, [95] boat temperature, and any subsequent thermal treatment [96] also changes ϕ by several degrees. The variation of ϕ with evaporation rate has been used to monitor the tilt angle of different LC composition. [97] The nature of the LC material, [93,95] its purity, [93] and—as shown in the case of cyanobiphenyls—the chain length, [85] also modify tilt values. We have observed wide variations of the tilt angle values in various cells where measurements have been made just after filling and subsequently after a period of stabilization: measurements on 11 cells have shown that, for ROTN 200, on obliquely evaporated SiO_x ($\theta : 85°$), the tilt angle values vary from 13° to 23°; however, after 500 hr, the different cells gave $\phi = 17.5° \pm 0.5°$. Despite experimental discrepancies, in general, rubbed layers give low tilt angles and rubbed polymers produce larger tilt angles (1°–5°) than rubbed inorganic surfaces (0°–2°), although 0° tilt angle has been measured on rubbed polyvinyl alcohol for a wide range of LC mixtures [95] and $\phi = 1°$ has been measured for an ester mixture aligned by polyamide–imide layers deposited on

TABLE VI

Indicative values of nematic director tilt angles on some typical aligning layers

Substrate	LC	Angle (°)	Method	Reference
Evaporated:				
SiO_x 63°	?	3° •	magneto capacit.	(102)
SiO_x 85°	5CB	27	moving isogyre	(96)
	6CB	29	moving isogyre	(96)
	6CB	29.4 ± 0.7	Δn	(110)
	7CB	31	moving isogyre	(96)
	7CB	24.1	magneto capacit.	(94)
	8CB	34	moving isogyre	(96)
	50CB	34		
	70CB	37		
	90CB	39		
	60CB	38		
	80CB	41	moving isogyre	(96)
SiO_x 85°	E8	25–27 (25 after 300 h)	magneto capacit.	(20)
SiO_x 82°	E7	25.3	magneto capacit.	(94)
	MBBA	23.3–26	magneto capacit.	(94)
	TN103	21.8	magneto capacit.	(95)
SiO_x 82°	TN200	15–22 (17 after 910 h)	magneto capacit.	(20)
	TN200	22.2	magneto capacit.	(95)
	TN403	22.7	magneto capacit.	(95)
	E7	25.4	capacitance	(104)
SiO_x 85°/60° 100 Å/0 — 30 Å	E7	25.3	capacitance	(103)
	E7, TN200	25 — 0	capacitance	(111)
SiO_x 60°/85° 100 Å/0 — 10 Å	E7	0 — 25	magneto capacit.	(41)
SiO_x 85 — 80°	(5CB/60CB)	0 — 33	magneto capacit.	(94)
84 — 74°	nSB	30 — 45		(102)
76 — 72°	nSB	15 — 25		
	?	3 — 9		
Rubbed:				
In₂O₃	E3	0.05	magneto null.	(93)
Glass	SB	0.5–5	capacitance	(41)
PVA	103.200. 403. E7	0	magneto capacit.	(95)
In₂O₃	E7	2.15 ± 0.1	magneto capacit.	(112)
NMAP silane	E3	0	magneto null.	(93)
Rhodiakermid	E3	0.95	magneto null.	(93)

SiO_2 rubbed with diamond paste. [89] A tilt angle of 2° has been measured for pentylcyanobiphenyl on rubbed glass as well as for a biphenyl mixture on rubbed glass and rubbed SiO_x layers evaporated at 60°C incidence. [95] SiO_2 layers rubbed with diamond paste align ester mixtures parallel to the substrate ($\phi = 0°$). [89]

Evaporation of metals or oxides obliquely to the substrate leads to layers which align LCs differently depending on the angle θ of the evaporation beam

with respect to the normal to the surface[44] (Figure 2). If $\theta < 45°$, parallel but nonuniform alignment is observed, but when $45° < \theta < 75°$ LC molecules align in a direction perpendicular to the incident beam with a tilt angle very close to zero. Tangential evaporation at $\theta > 75°$ results in the nematic director being oriented towards the source at an angle of approximately 15°, increasing to 25° as θ increases from 75° to 88°.[48,102] When θ is 72°–75° the LC molecules lie parallel to the substrate plane, with the director axis perpendicular to the plane of incidence of the evaporation beam, at a low tilt angle (3°–9°).[102] These values have been widely confirmed by numerous authors and repeatedly obtained in industrial practice for all of the practical LC mixtures.

Tangentially evaporated MgF$_2$ gives similar results but with smaller tilt angles than SiO$_x$ for the same angle of evaporation.[15] Oblique evaporation of CaF$_2$ is reported[12] to produce homeotropic alignment ($\phi = 90°$) when $\theta < 45°$, $\phi = 75°$ for $45° < \theta < 70°$ and $\phi = 60°$ for tangentially evaporated layers ($\theta > 75°$). Surfactants, some silanes and polymers produce homeotropic alignment. Rubbing and tangential evaporation of oxides give low tilt angles while oblique evaporation induces a 25° tilt angle. When other tilt angles are desired, any combination of high and low-tilt-angle-producing
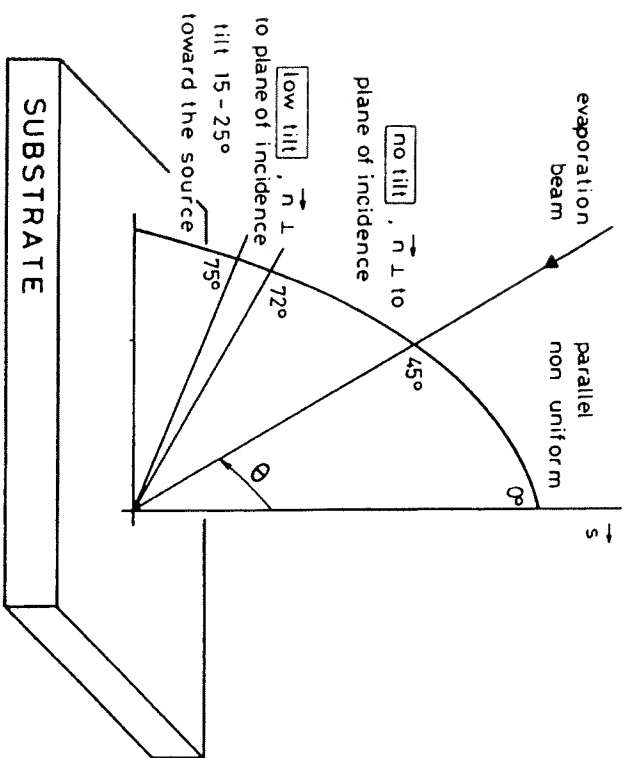

FIGURE 2　LC nematic director orientation induced by evaporated silicon oxide (or magnesium fluoride). Depending upon the angle of incidence of the evaporation beam different orientations are observed.

methods can be employed. The tilt angle of a tangentially evaporated layer may be lowered by rubbing[98] or by crossed evaporation of two layers of different thickness at the same angle of incidence θ.[99] Deposition of a very thin (less than 5 Å) layer of SiO$_x$, evaporated at an angle of 6° from the substrate ($\theta = 84°$), on to a layer deposited at 60° incidence, after 90° rotation of the plate, gives a tilt angle of 0° to 6°.[102] By employing the reverse order[104] i.e., an initial evaporation of a 50 Å SiO$_x$ layer at an incidence angle of 5°, followed by a rotation of 90°, and 100 Å evaporation of SiO$_x$ at 80°, low tilt angles (5°) are obtained with the LCs E7 or ROTN 200. Variation of the layer's thickness allows tilt angles to be controlled from 0° to 30°. Variation of ϕ from 0 to 45° for E$_3$ has been obtained by simultaneous evaporation of SiO from two sources.[105] Electron gun deposition of an initial layer, 350 Å thick, at 6° incidence, followed by a 20–50 Å thick layer deposited at 30° without rotation of the substrate, gives a 6° tilt angle.[102] Variations of ϕ from 11° to 3° can be produced by monitoring the thickness of the second layer. SAIBE SiO$_2$ covered with long chain alcohol allows tilt angles to be varied from 75° to 90° depending on the surfactant chain length,[45b] while plasma deposition of an 8 Å Teflon layer on to 70° evaporated SiO$_x$ gives a tilt angle of 15°.[106]

A SiO$_x$ layer evaporated at a low angle, which would normally result in a tilt angle of 25°, when treated with a homeotropic aligning layer of lecithin, orient the LC at the complementary angle of $\phi = 65°$ (Figure 3), as has been observed when this layer is treated with octadecylammonium bromide,[44] or deposited on glass cleaned with sulfochromic acid.[108] Evaporation of two dissimilar materials, such as gold and indium oxide, on adjacent sides of the grooves of a wavy surface gives a LC alignment slightly tilted from the normal for LC mixtures containing a homeotropically aligning surfactant.[107]

Orientation of thin LC layers may be obtained with the nematic director oriented in any direction from $\phi = 0$ to 25°–35° and 60° to 90° by a suitable aligning layer (Diagram 1).
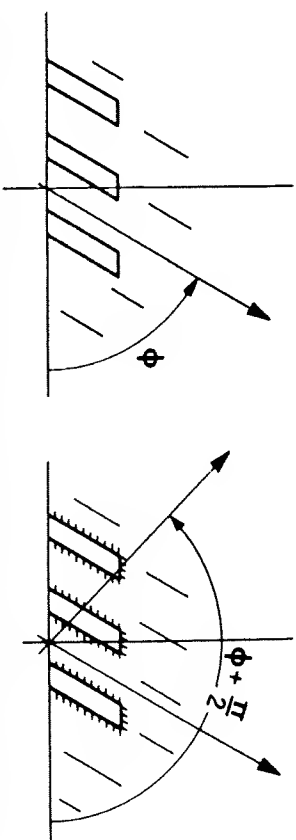

FIGURE 3　Where an inorganic surface produces an average orientation of the LC molecules at an angle ϕ, treatment by an homeotropic aligning surfactant leads to an orientation at the complementary angle.

II ALIGNMENT MECHANISMS OF NEMATIC LIQUID CRYSTALS AND THEIR MIXTURES

Evaluating the various alignment methods reviewed in §I aided greatly in clarifying some general guidelines for LC–surface interactions.

The difficulties encountered, while attempting to obtain meaningful experimental data, due to ill-defined substrates, LC decomposition, and surface chemistry misconception have hindered progress in the understanding of the subject. LC molecules are composed of an aromatic core, an alkyl chain and a polar group, thus giving rise to complex dispersive polar and hydrophobic interactions.

II.1 Physicochemical interactions

II.1.1 The Friedel–Creagh–Kmetz rule

An old, but neglected study of the alignment of LCs (mainly azoxy compounds) on freshly cleaved crystals[23] suggested that the orientation of the LC molecules was determined by their physiocochemical interactions: of 80 studies of LC alignment on crystal surfaces, 77 showed parallel orientation. If, however, a hole was drilled in the solid substrate, homeotropic alignment ensued in the suspended film. This led to the conclusion that LC films aligned parallel to a solid substrate if any interaction occurred and homeotropically in the absence of interactions.[10]

Solid–liquid surface interactions are phenomenologically described by the surface tensions of the solid substrate, γ_S and of the liquid γ_L. γ_L is a macroscopic description of the strenght of the LC–LC interaction while γ_S describes the solid surface excess energy.

Thus, the above observations may be stated as[6]

$$\gamma_S < \gamma_{LC} \longrightarrow \text{homeotropic alignment}$$
$$\gamma_S > \gamma_{LC} \longrightarrow \text{parallel alignment}$$

This empirical rule has been widely supported by experimental data, although not all results are in agreement. We will call it the "Friedel–Creagh–Kmetz" (FCK) rule.

II.1.2 Surface tension

II.1.2.1 Liquid crystal surface tension

In order to have thermodynamic significance, the LC surface tension, γ_{LV}, should be measured with the LC in equilibrium with its vapor. Most of the available data are relevant to an air–LC interface, γ_{LA}. Although the precision

90

(CaF₂?)
Surfactants
Polymathylsiloxanna
Fluorinated Polymers

Tangentially evaporated CaF₂?
longchain alcohol on SAIBE SiOₓ
Surfactants on tangentially evaporated layers
plasma polymerised fluorinated film on tang. evap. layers
(one of the method below + surfactant)

65 ——— Lecithin or DMOAP adsorbed on Si Oₓ evaporated tangentially

60

25   Si Oₓ, MgF₂ evaporated at θ < 75°C

15   C₂F₄ plasma polymerised on Si Oₓ evaporated at θ < 75°C

double evaporation

10   Si Oₓ evaporated at 72 < θ < 76°C

5   Rubbed Polymers

3   Rubbing of inorganic layers obliquely evaporated Si Oₓ. MgF₂ (45 < θ < 75°C)
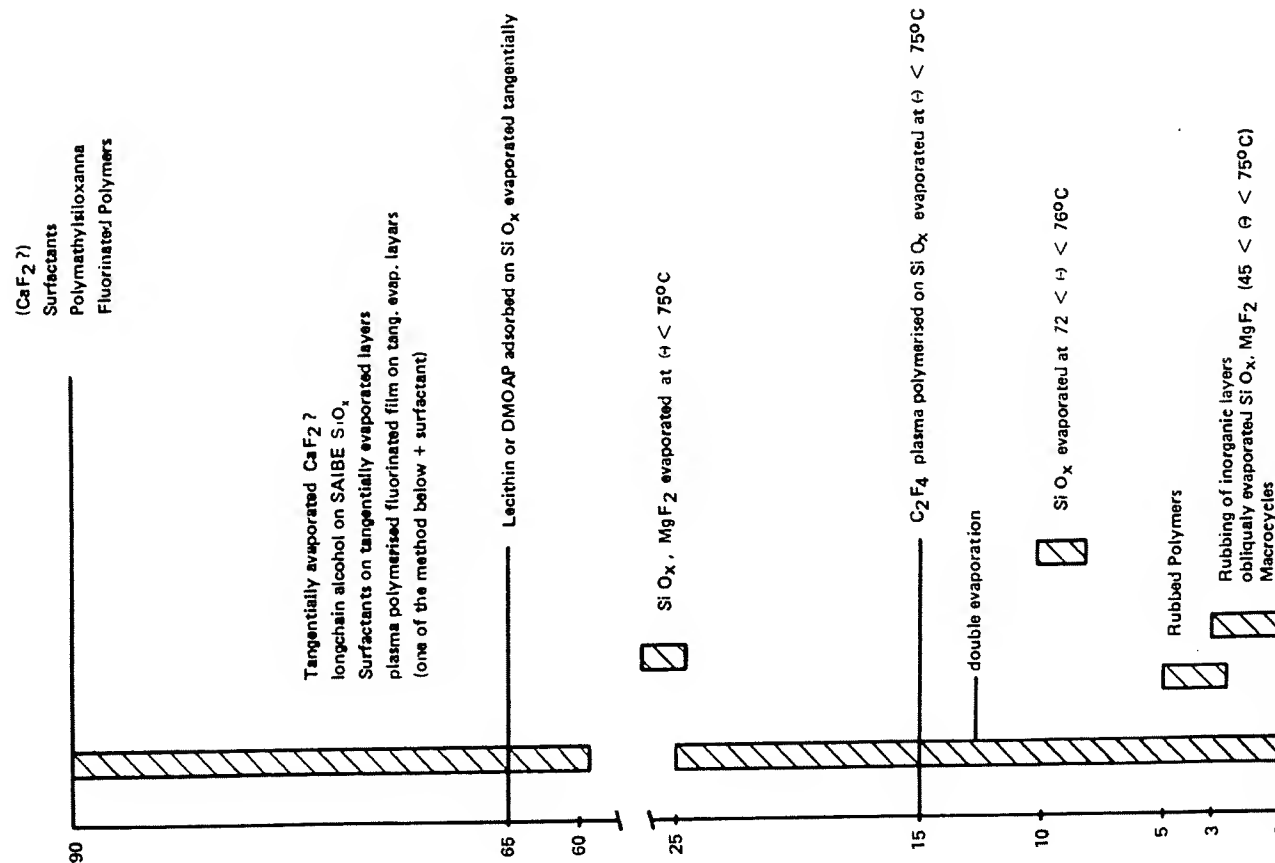   Macrocyles

0

DIAGRAM 1   Tilt angle of the LC nematic director produced by different surface treatment.

of the different methods used to measure the LC surface tension should be 10^{-4} J m^{-2}, comparison of the published values, (Table VII), shows a dispersion, that may amount to 30% with the same method. This is probably due to non-equilibrium conditions and/or atmospheric contamination of the LC (for the influence of different methods see § II.1.10).

The surface tension of MBBA has been found impossible to measure precisely,[113] as the LC interface drifts continuously. LC surface tensions are of the order of 25-40 erg/cm^2.

II.1.2.2 Anisotropy of the surface tension of a LC

The existence of a liquid crystalline state implies an anisotropic intermolecular potential. As surface tension results from the excess energy of the molecules at the surface, it would be expected to vary according to whether the LC molecules were oriented parallel or perpendicular to the surface.

Calculations of the surface tension anisotropy, taking into account only van der Waals interactions[118,119] leads to $\gamma_{\parallel} < \gamma_{\perp}$. This calculation is applicable to LCs of negative $\Delta\epsilon$ as their long axis dipole moment ($\mu_{\parallel}$) is weak and the off axis dipole moment ($\mu_{\perp}$) averages out. As a result the LC molecules lie flat at the LC-air interface (e.g. PAA, Ref. 115).

MBBA has $\mu_{\parallel} = 0.4$ D and is slightly tilted[114] at the free surface, which could be due to the angle between the molecular axis and the diple moment. For LCs of strong polarity, experimental observations show that the LCs align normal to the free surface[120]; thus $\gamma_{\parallel} < \gamma_{\perp}$, which contradicts the theoretical evaluation of dipole interactions in LCs.[119] The calculated value of $\gamma_{\parallel} - \gamma_{\perp}$ is 7×10^{-3} J m^{-2} for PAA (Ref. 116) while $\gamma_{\parallel} - \gamma_{\perp}$ of the order of 5×10^{-6} J m^{-2} (Ref. 75, 120) is obtained from experimental observations (see Table VII). The Kirkwood-Buff approximation leads to $\gamma_{\parallel} - \gamma_{\perp} = \gamma_0 (S/9)$ [$10 - 7S/6$] (Ref. 119)† with the previously mentioned limitations.

It has been suggested[5] that a situation could exist where the solid substrate surface tension, γ_S, has an intermediate value $\gamma_{\parallel} < \gamma_S < \gamma_{\perp}$, leading to a tilted orientation of the nematic director. Experimental values are much too small to explain the observed tilted alignment of MBBA on glasses onto which fatty derivatives of medium chain length (C_6-C_{10}) have been adsorbed ($\gamma_S \sim 26 \times 10^{-3}$ J m^{-2}). Such an effect would require $\Delta\gamma \geq 8 \times 10^{-3}$ J m^{-2} as calculated from theory. Further work seems to be required to ascertain the real order of magnitude and its relation to various LC classes.

II.1.2.3 The surface tension of solids

The surface tension of a solid cannot be measured directly. Calculation of the excess surface energy from the energy of the broken bonds necessary to create

† Reference 113 suggests that after correction of errors in the evaluation of the integral, $\gamma_{\parallel} - \gamma_{\perp} = \gamma_0 (S/3)(5 - 19/32 S)$.

a surface, give values of 0.5 to 5 J m^{-2}[121]; these values refer to the solid-vacuum interface, γ_S^0.

As soon as the solid surface is brought into contact with air, atmospheric constituents strongly adsorb onto the surface, lowering the surface tension from the uncontaminated value of the "surface pressure" π_0.

The solid-air interface has thus a surface energy,

$$\gamma_{SA} = \gamma_S^0 - \pi_0,$$

where π_0 is approximately 0.1 J m^{-2}.[128]

Due to the fact that the solid surface chemical state is poorly defined, it has been suggested that the oxide surfaces should be considered as covered by a thin layer of water, with $\gamma_{SA} = 7 \times 10^{-2}$ J m^{-2}.[117]

Cleaning procedures, as well as further thermal treatment, will modify the properties of a solid surface. In the case of silica layers, heating will desorb the physically absorbed water at around 150°C and following this will be condensation of surface hydroxy groups between 170°C and 400°C, to form oxygen bridges. Above 400°C, the oxygen bonding becomes irreversible, and above 750°C, the silica surface become irreversibly hydrophobic.[122] Irreversibly absorbed water causes TiO$_2$ surfaces to become hydrophobic.[123]

In general, hydrophobic oxide surfaces consist of areas incapable of specific molecular interactions.[123] Complete removal of the specific interactions on inorganic substrates supposes thermal treatment at very high temperatures, which are not suitable for glass cells.

Tin oxide thin films, formed by CVD are hydrophobic; acid cleaning renders them hydrophilic.[20]

Even in the case of a uniform solid surface, its surface energy is difficult to predict. The same oxide may show different surface energies, depending on preparation conditions, subsequent thermal treatment, (which is unavoidable during display sealing) and cleaning procedures. For inorganic solid surfaces, however, γ_{SA} is greater than 4×10^{-2} J m^{-2}.

To reliably establish the validity of the FCK rule it would be necessary to measure the surface tension of the solid in equilibrium with the LC vapor (γ_{SV}), at the saturated vapor pressure. In this case π_0 would be the pressure of the absorbed LC film. It is often claimed that LC alignment is not understood; the situation is not worse than that of surface chemistry.

II.1.3 Solid-liquid crystal contact angle

II.1.3.1 The contact angle

When a liquid is deposited on a surface it often happens that it remains as a drop. The angle θ_{SL}, between the edge of the drop and the surface is related to γ_{LV}, γ_{SV} and the interfacial energy, γ_{SL}, by the expression

$$\gamma_{SV} \cos \theta_{SL} = \gamma_{SV} - \gamma_{SL}. \tag{3.1}$$

Surface tension γ_L of some nematic LCs[*]

X	L.C.	γ_L 10^{-3} Jm^{-2}	Ref.	Method	Remarks
SCHIFF'S BASE	MBBA	38	117	—	• One group of value 38 ± 2 an other group 28 ± 2 • γ_L of MBBA impossible to measure accurately (113) • Effect of impurities is slight (38) • MBBA aligns nearly ⊥ at the free surface (114 b)
		38 ± 3 (23°C)	114	VI	
		35.8	38	III	• $\gamma_\parallel < \gamma_L$
		35.3 (25°C)	116	III	$\gamma_\parallel = 34$ $\gamma_L = 26$ (5)
		35.3	115	V	
		34	37	II	• $\gamma_d = 29$ $\gamma_p = 9$ (117)
		34	34	I	• $\gamma_d = 33$ $\gamma_p = 1$ (37)
		32 – 34	6	II	corr — uncorrected
		32.6*	7	II	• $\gamma_L = 28.8$ corr. Harkins and Jordan (1)
		30	5	I	
	80 MBBA/ 20 BBCA	36.5	37	II	• $\gamma_d = 34$ $\gamma_p = 1.5$ (37)
AZOXYS	PAA	39.6 ± 0.4 (120°C)	117 a	II	• PAA aligns ∥ to the free surface ⇒
		39 (120°C)	117 b	VIII	$\gamma_\parallel < \gamma_L$
		38.9	115	V	
		38.8 ± 0.4	138	VII	
		38 ± 4	114 b	VI	• $\gamma_\parallel^d$ (calc) = 37.8 $\gamma_\perp^p = 44.6$ (118)
		37.9	117 c	VIII	
		37 (120°C)	116	III	
	PAP (158°C)	29.1	117 b	VIII	
		29.2	115	V	
		29.8	117 a	II	
STILBENE	MBAB	37.3	38	III	
	BECS	35.7	38	III	
ESTER $\Delta \epsilon < 0$	MPPB	24.5	34	I	
$\Delta \epsilon > 0$	HCPB	27	34	I	
	ROTN 103	27.5 ± 0.3 (22°C)	20	III	
TOLANES	MPT+PHT	25	34	I	not aligned on plasma PTFE ⊥ (34)
BIPHENYLS	5 CB	40	133	I	• C.B. aligns ⊥ to the free surface ⇒
		34.4	84	II	$\gamma_\parallel > \gamma_L$
		32 ± 0.5	20	III	
		30	32	I	•
	8 CB	28.1 (31.5°C)	113	I	• (Plates treated for homeotropic alignment)
		27.9 (20°C)	113	I	• $\gamma_L = 30$
		26.2 (41°C)	113	I	
	E 7	29.3 (22°C)	20	III	
	E 8	30.6 ± 0.2 (22°C)	20	III	
PHENYLCYCLOHEXANE	ZLI 1132	31 ± 0.5 (22°C)	20	III	• Difficult to align homeotropically (20)

[*] Methods: I, wilhemy plate; II, de Nouy ring; III, hanging drop; IV, contact angle; V, capillary; VI, light scattering spectrum; VII, radii of curvature; VIII, maximum bubble pressure.

At equilibrium it should not matter whether the drop is deposited on the surface (advancing angle) or whether it is formed by pulling out a film of the liquid (receding angle).[124] On a LC drop, in practice, variations in θ_{SL} as great as 50° may be observed, and experimentalists generally choose the advancing angle. When studying hydrophobicity, the receding angle is a better characterization of the surface.

The existence of hysteresis has been attributed to contamination of either the liquid or the solid, rough surfaces or absorbed surface film immobility.[121]

II.1.3.2   *The contact of a liquid crystal with a solid*

Whatever the method used to measure the contact angle of a LC drop on a solid, observations are hampered by the continuous drift of θ_{SL}. On the one hand the absorbed atmospheric constituants have to exchange with the LC molecules; on the other hand the elastic energy of the misaligned layers is weak and the evolution of surface attached disclinations is slow. Four days have been selected as the time necessary for a LC to attain equilibrium with an adjacent surface when making accurate measurements.[113] Liquid crystal hydrolysis and/or oxidation under the influence of both UV light and oxygen[45c] complicate experimental studies. Frequently the edges of LC drops are observed to be homeotropically aligned after 10 days, due to the formation of polar decomposition products.

On substrates which induce parallel LC alignment, the viscous flow of the LC tends to determine the direction of alignment, but many defects are formed and they evolve constantly, resulting in constant movement of the LC drop. It seems that reliable values can only be obtained with carefully controlled experimental conditions which have rarely been the case in the published studies.

II.1.4   *The critical surface tension of a solid*

A useful empirical parameter has been proposed to characterize a solid surface. It has been observed that the contact angle θ_{SL} of homologous alkanes varies linearly with the liquid surface energy. Extrapolation to $\cos \theta_{SL} = 1$ led to a critical value γ_C which was characteristic of the solid employed.[128] From Eq. (3.1)

$$\gamma_{LV} \cos \theta = \gamma_{SV^0} - \gamma_{SL}$$

and, therefore,

$$\gamma_C = \gamma_{SV^0} - \gamma_{SL}.$$

The introduction of a critical surface tension is only valid inasmuch as the values γ_{SL} and π_0 ($\gamma_{SV^0} = \gamma_{S^0} - \pi_0$) of different liquids are constant. If this is the case for polymers and nonpolar liquids, the use of polar liquids to measure

γ_C may cause large variations of the extrapolated value. Therefore, γ_C values for polar oxide surfaces relate to the nature of the surface and the choice of the solvents. The following observations indicate that in these cases γ_C is not a useful parameter for the characterization of LC–oxide interactions.

- The critical surface tension of fused silica is $\gamma_C = 78 \times 10^{-3}$ J m^{-2}.[125]
- On SiO$_x$ tangentially evaporated films, γ_C has been measured to be approx. 38×10^{-3} J m^{-2} after correcting for surface roughness[126] with an anisotropy which depends on whether the edge of the drop is parallel or perpendicular to the evaporation direction.
- Normal evaporation is reported to produce films of $\gamma_C = 48.7 \times 10^{-3}$ J m^{-2} while obliquely evaporated layers show 48.7×10^{-3} J m^{-2} < γ_C < 55.9×10^{-3} J m^{-2} for evaporation angles between 0° and 60°.[127]
- On SAIBE etched SiO$_2$ surfaces, values of γ_C as low as 24×10^{-3} J m^{-2} have been measured[45a] which is nearly the critical surface tension of water [γ_C(H$_2$O) = 22×10^{-3} J m^{-2}].[45c]
- Atmospheric humidity causes the critical surface tension of glass to vary from between $\gamma_C = 75 \times 10^{-3}$ J m^{-2} for dry glass, to $\gamma_C = 30 \times 10^{-3}$ J m^{-2} at 100% humidity.
- Although water has a γ_C value of 22×10^{-3} J m^{-2}, LCs ($\gamma_C = 3 \times 10^{-2}$ J m^{-2}) do in fact align parallel on water.[120]

As developed in the following paragraph γ_C is equal to the solid surface tension γ_{SV^0} when the ratios or polar and dispersive interactions of both phases are equal. For this reason the critical surface tension of polymers may be employed to give a qualitative description of polymer–LC interactions. Measurements made on plasma polymerized films[34,37] showed acceptable agreement with theory, although some unexpected results were observed, i.e., tolans ($\gamma_{LC} \sim 22 \times 10^{-3}$ J m^{-2}) were not aligned homeotropically by a sputtered Teflon layer ($\gamma_C \sim 18 \times 10^{-3}$ J m^{-2}).[34]

Adsorbed surfactants reduce the solid surface tension. Fatty acids or their derivatives (alcohols and amines) exhibit a continuous range of γ_C values with alkyl chain length[5,75] but reported relations to LC alignment are somewhat conflicting (Figure 4). The same discrepancies are observed with alkyl trimethyl ammonium bromide derivatives.[75] The influence of the surface coverage (or packing density) is of the utmost importance[8] and consideration of γ_C is generally misleading (see paragraph 18).

The FCK rule has generally been quoted[1,6] using γ_C in place of γ_S, i.e.,

$$\gamma_C < \gamma_{LC} \longrightarrow \text{homeotropic}$$
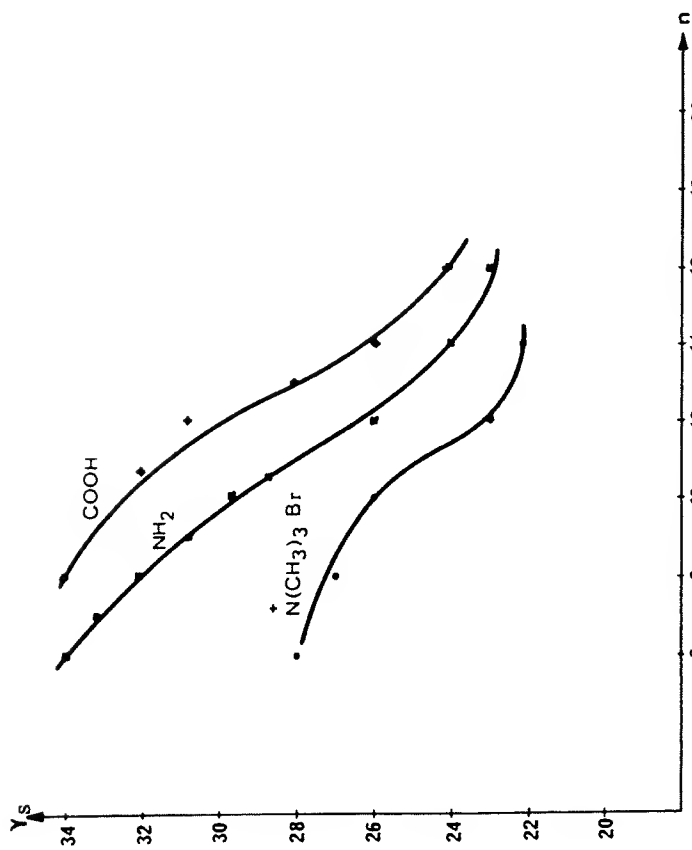$$\gamma_C > \gamma_{LC} \longrightarrow \text{parallel alignment}$$

FIGURE 4   Variation of the surface tension of surfactant treated glass surfaces with increasing carbon content of the surfactant alkyl chain. [● from Ref. 75a, × Ref. 5a + Ref. 56].

and it is, therefore, not surprising that it encountered strong criticism. Compared to the expression of § II.1.1, where $\gamma_s = \gamma_s^0 - \pi_0$, it is evident that the above inequality employs values that are relevant to nonpolar solvents, to describe the behavior of LCs which have to be highly polar for practical application.

II.1.5   The polar and dispersive components of surface tension

Surface interactions are long range forces; either dispersive (van der Waals) forces, dipole–dipole interactions or double layer interactions.[121] These contributions are considered additive and the surface tension $\gamma_i(i = s$ or $l)$ may be written as the sum of the dispersive γ_i^d and polar γ_i^p contributions,

$$\gamma_i = \gamma_i^d + \gamma_i^p.$$

Let d_i and p_i be the ratios of dispersive and polar contributions to the surface tension: $d_i = \gamma_i^d/\gamma_i$, $p_i = \gamma_i^p/\gamma_i$. It is shown that the critical surface tension γ_c

is $\gamma_c = \phi\gamma_{sv^o}$ where $\phi = \sqrt{d_L d_s} + \sqrt{p_L p_s}$. When $d_i = d_s$, which implies $p_L = p_s$, $\phi = 1$ and $\gamma_c = \gamma_{sv^o}$.

Thus the empirical method of estimating γ_c may result in a value that agrees well with γ_s^d rather than the solid surface tension γ_{sv^o}.[129] Recent work on plasma copolymerized films with different γ^d and γ^p values[37] shows the relation of these considerations to nematic LC alignment.

II.1.5.1   Polar interactions of LCs and surfaces

The interactions between the dipoles of LC molecules and the charged surfaces of oxides or ionic surfactants are certainly very important in the formation of the first surface layers, although theoretical understanding of the problem and the experimental data are poor. The effect of surface polarization has been demonstrated in the case of MBBA,[130] for which it was suggested that the MBBA molecules orient with their dipoles towards acid treated glass, but with their butyl chain towards surface cetylammonium bromide monolayers on glass.

In addition, the surface dipoles of sputter etched indium oxide have in some (but unreproducible) cases been observed[131] to align LCs of negative dielectric anisotropy parallel to the substrate, but positive LCs perpendicular to it. The same behavior is observed with surfaces treated with dicarboxylate[78b] chromium complexes, suggesting that only part of the acid group is absorbed onto the substrate. The polar interaction of MBBA with a humid glass substrate,† where $E_s = 4.35 \times 10^9$ V/m, have been shown[132] to be accounted for through the surface electric field, E_s (Table VIII) as the polar part W_a of adhesion energy. W_a is related to the LCs molecular dipole through

$$W_a p = \delta\mu E_s \qquad (\delta \text{ effective dipole density})$$
$$(\mu \text{ effective dipole moment}).$$

In view of this the existence of a double layer (§ II.1.6) should be considered.

II.1.5.2   Dispersive interactions of LCs and polymers

As already mentioned, nonpolar surfaces offer an important simplification in the theoretical description of liquid–solid interactions as the polar term becomes negligible regardless of the character of the liquid molecules. Most organic compounds as well as Liquid Crystals and polymers have $d > p$.

Denoting γ_i^d as the dispersive component of the surface tension, the

---

† This work has been extended to 5CB by these authors in Ref. 133 but the observation of homeotropic alignment of 5CB on glass cast some doubts on their conclusions.

Electrostatic field strength E_s and dispersion energies γ_s^d for some inorganic substrates (from Ref. 132)

TABLE VIII

Substrate	E_s	$\gamma_s^d (10^{-3}\ J\ m^{-2})$
Rutile	8.1×10^9	145
Rutile (bare)	$6. \times 10^9$	125
Al_2O_3-SiO_2 coated	9.6×10^9	135
CaF_2	7.5×10^9	105
SiO_2	3.3×10^9	105
Al_2O_3 (40 Å on Al)	5.7×10^9	335
Carbon black	2.1×10^9	105
Teflon	0	25

ᵃ Calculated from the heat of adsorption E_a (J m^{-2}) of the powders in solvents of different dipole moment μ. $E_s = E_a/\mu$, E_s in V m^{-1} per cm^2 of surface.

Girifalco, Good, Fowkes, Young equation (GGFY) permits the calculation of the interfacial energy γ_{SL}:

$$\gamma_{SL} = \gamma_S + \gamma_L - 2\sqrt{\gamma_S^d \gamma_L^d}$$

For LCs, γ_L^d is of the order of 10^{-2} J m^{-2}. Polyethylene has $\gamma_s = \gamma_s^d = 3 \times 10^{-2}$ J m^{-2} thus γ_{SL} 27 × 10^{-3} J m^{-2}.

> In general the alignment of LCs on polymers is well described by the FCK rule. [34,37]

II.1.6 *The "smecticlike" interfacial layer*

The interfacial layer between a solid and a liquid gives rise to a charge separation, which can be well described in terms of a double layer (DL) which consists of a compact ordered monolayer firmly bound to the substrate, followed by a layer of diffuse charges. This DL has not been studied in LCs where the electric charge density is not known, but its existence has been theoretically [134] predicted and is supported by electrical measurements. [135,136] It could be relevant to the higher order parameter of the interface between nematic LCs and solids or gases.

Practical LCs being ionically very pure the compact layer will be the main component.

Many experimental observations imply that the surface layer has a higher order than the bulk. Microscopic observation of nematic layers squeezed between glass slides suggested that there is a thin interfacial layer firmly bound to the glass substrate, [10] which determines the orientation of the adjacent layer.

Infrared spectroscopy indicates that the excess order depends upon the nature of the substrate (glass, In$_2$O$_3$, polysiloxane). [13b] Additional evidence for the existence of a DL comes from observations of a film of the LC 5CB, less than 250 Å thick pulled apart in air. Such a layer has the appearance of a smectic layer with an order parameter, S_φ, 1.005 times that of the bulk value S_c. [120]

Also, whereas the surface tension of a normal liquid decreases when the temperature increases, the reverse has frequently been observed with nematic LCs. [113] ‡ This effect could be explained by a higher surface order parameter S_φ: γ_{SL}^0 is the surface tension of the isotropic LC, then the surface tension $\gamma^0(S)$ of the oriented layer is

$$\gamma^0(S_\varphi) = \gamma_{SL}^0 - \alpha S_\varphi, \text{ with } \alpha \sim 2 \times 10^{-4}\ J\ m^{-2}.$$

Optical measurements clearly show the higher birefringence of the interfacial layer, e.g. $S_a = 0.5$, and $S_e = 0.4$ (Ref. 137) for the LC 7CB. Theoretical investigations of surface alignment have to take into account this more ordered surface layer. [11] The structure of this first compact layer, which also determines the surface pressure of the adsorbed LC vapor, influences the orientation of the nematic crystal layers throughout the bulk of the LC, as does a layer of smectic liquid crystal deposited on a substrate. [90]

The dispersive interactions of LCs with solid surfaces are strong. For metals and oxides γ_s^d is about 0.13 J m^{-2} and around 3 × 10^{-2} J m^{-2} for polymers. The dispersive component of LC surface tension has been found predominant over polar interactions $\gamma_L^d \sim 3 \times 10^{-2}$ J m^{-2}, the interfacial energy is for most LCs essentially dispersive leading to the parallel alignment of the alkyl-aromatic part of the LC molecules. [124] The polar contribution of the solid–liquid interactions will favor the parallel alignment of negative Δε LCs while it will lower the anchorage of positive Δε LCs. [13] Experimentally it is observed that cyanobiphenyls are more easily oriented homeotropically than negative esters. Silicone layers, for example, orient high positive Δε LCs homeotropically but not phenyl cyclohexanes.

During the initial contact between the LC and the surface, the smecticlike layer forms. Defects spreading out through the LC film are initiated by some surface irregularities. Often they evolve in time as adsorbed atmospheric components exchange with LC molecules.

The energy confined in the smecticlike layer is higher than can be added to the LC film by mechanical, electrical or thermal action. Once it is formed, the substrate enclosing the LC film may be twisted without changing the interfacial ...

‡ We have not reviewed the influence of temperature on LC surface tension and alignment as our own work on the subject is insufficient on the one hand and published results too contradictory on the other hand. Some indications may be found in Refs. 3 and 111.

cial layer.[54] Also its orientation at the free surface is not changed by applying a magnetic field.[138] Consequently, the physical properties of LCs are weakly affected by the very first layer (see also § II.3).

II.1.7 Nonuniform coverage

When an aligning layer is deposited nonuniformly on a substrate, both the exposed substrate and the aligning layer will influence the LC alignment. If the substrate and the alignment layer tend to induce different orientations of the LC molecules, tilted alignment will be observed. The theoretical computation of the equilibrium director orientation shows that different tilt angles will be observed, depending on relative values of the LC elastic constants.[139] This situation is likely to occur in the case of absorbed surfactants at low coverage[140] or when hydrolyzed chloro or amino silanes form polymeric nodules on the surface,[141] or when very thin polymeric[91] or evaporated films are deposited on the substrates.[132] In these cases one is dealing with a parallel-orienting substrate presenting patches of homeotropic-aligning layers.

Alternating stripes of surface materials, one giving a homeotropic and the other giving parallel alignment produce a bulk average tilt angle of 45°.[139] When the bend constant, K_{33}, is larger than the splay constant, K_{22}, theoretical calculations indicate that the angles will be less than 45°, while it will be greater in the inverse case.

II.1.8 Alignment by surfactant

Almost every known class of surface active agent has been observed to influence LC alignment (see § 3, Part I).

In most cases LCs are aligned homeotropically by long chain surfactants adsorbed on inorganic substrates. Because they lower surface tension, it has often been thought that the FCK rule should apply and explain the observed alignment.

Superficial films of adsorbed molecules are known to exist in four states[121]: the G (gaseous) state corresponds to a weak coverage. Higher coverages lead to an L (liquid) state either expanded (L_1) with an average surface of 50 Å^2 (40–70 Å^2) covered by each adsorbed molecule as for long chain polar compounds or a condensed (L_2) state where the surface covered by each adsorbed molecule is about 22 Å^2 (cetyl alcohol).

Dense layers create S (solid) films with an area of 20.5 Å^2. Some surfactants produce both the L_1 and L_2 state with an intermediate (I) phase. The properties of superficial films of phospholipids (e.g., lecithin) have been explained as due to their liquid crystalline organization (Figure 7).

In order to obtain monolayers of known structure, a Langmuir balance is generally used,[124] but the technique is tedious and difficult to apply in industry. The normal practice, therefore, is to adsorb layers from solution and relate

their structure to that of the Langmuir monolayer. The retraction method has been shown to form good monolayers[142] although they present slight differences in their properties compared to the former,[143] probably because of the incorporation of solvent into the layer.

The investigation of the structure of layers adsorbed from solutions is still in progress[144] and their are few cases where it is complete. In Figure 4 we have gathered experimental values of the critical surface tension of glass covered with adsorbed layers of fatty derivatives of increasing chain length. If the results are assumed to indicate the influence of the carbon content of the chain on the substrate interfacial energy, the relation of LC alignment is not so clear, as in every case MBBA is aligned parallel to the substrate in the upper portion of the curves and homeotropically in the lower one. "On the completion of the adsorbed monolayer on the surface of a solid, the orientation of hydrocarbon molecules is parallel to the substrate as shown in Figure 5, whereas polar-nonpolar molecules on a polar solid stand upright as shown in 5b. However, if plenty of area is available, as in a dilute film, the polar-nonpolar molecules also lie down. As the film thickens and becomes multimolecular, the orientation in the first layer of polar-nonpolar molecules preserves the perpendicular type of orientation. If the vapor becomes saturated and the liquid of the film wets the solid, the film is relatively thick (about seven molecules thick for water at 25°C) and the molecules in the surface of the film have approximately the same orientation as in the surface of the liquid itself".[124]

In addition, the packing density of fatty acids depends on their chain length.[142,145] This could be an explanation for the tilted alignment of MBBA on surfaces covered by retracted layers of C_{10}–C_6 fatty derivatives.
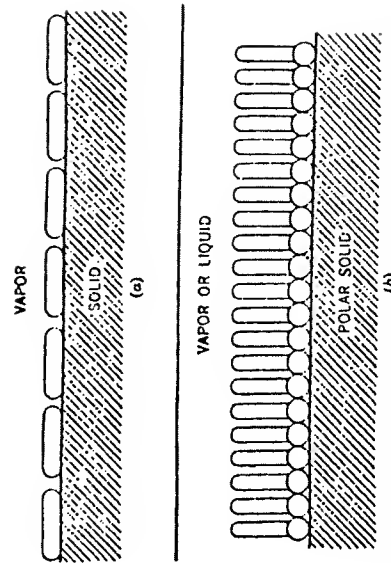

FIGURE 5 Orientation of molecules in complete monolayers. (a) Hydrocarbon molecules. (b) Polar molecules on the surface of a polar substrate. (From Ref. 124).

J. COGWARD

Liquid crystal alignment may be understood from the surfactant's adsorption isotherms. Cetyl ammonium bromide (CTAB) solutions in water adsorb parallel to the substrate at low concentration while at higher concentration the surfactant molecules orient perpendicular to the substrate.[8] MBBA deposited on these layers takes the surfactant orientation (Figure 6).

Phospholipids (e.g., lecithin) monolayers have different structures (Figure 7) depending on their surface pressure, retraction on glass substrate keeps the layer structure.[147] On tightly packed layers, cyanobiphenyls show a tilted orientation whereas on layers of lower packing density homeotropic orientation is observed. Experimental evidence leads to the conclusion that LC molecules are imbricated in the surfactant layer.[148]

The efficiency of a surfactant to align LCs also depends on its molecular structure; cyanobiphenyls are much more easily aligned homeotropically than phenylcyclohexanes.

As silanes may form covalent bonds with oxide substrates one would expect more permanent effects to result from the adsorption of long chain silane derivatives.

Very little is known about the structure of silane monolayers. Polymeric nodules very often form on the surface[141] but can be avoided by anhydrous conditions.[142]

Octadecyltrichlorosilane (OTS) adsorbed from nonaqueous solutions forms dense monolayers.[144] Carbon-14 counting shows a surface density of 1.5×10^{14} mole/cm^2, as compared to 5×10^{14} for ^{14}C arachidic acid, which corresponds to close packing of Si–O bonds associated in three dimensions.[150] All our test LCs aligned homeotropically on oxide substrates covered with OTS. 3-(2-Aminoethyl)aminopropyl TMS, used to facilitate homogeneous alignment (Table V), is also known to be densely adsorbed on tin oxide from a 5% solution in toluene.[149]
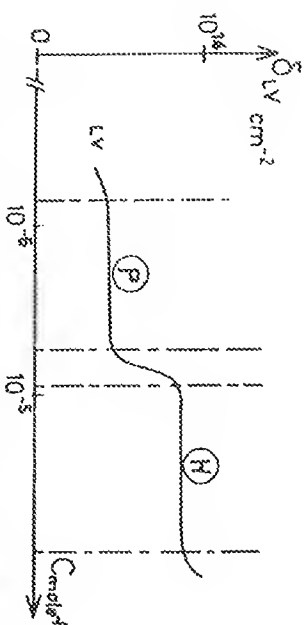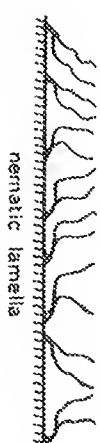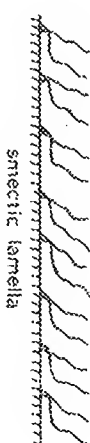
$\hat{\delta}_{LV}$ cm^{-2}

10^{14}

LV

P

H

$C_{mole/l}$

10^{-6} 10^{-5}

FIGURE 6 Variation of the superficial density (δ_{SV}) of adsorbed cetyl trimethyl ammonium bromide (CTAB) with its concentration in solution. (From Ref. 157).

ALIGNMENT OF LIQUID CRYSTALS

GASEOUS (G) STATE

LIQUID (L) STATE

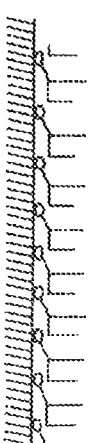smectic lamella

nematic lamella

SOLID (S) STATE

FIGURE 7 Schematic representation of phospholipid (e.g., lecithin) monolayers. (From Ref. 146).

II.1.9 Surface hydrolysis

Liquid esters have surface tensions of $28-30 \times 10^{-3}$ J m^{-2} and should spread on high energy surfaces such as metals and oxides. Whereas they do spread on metals they do not always do so on glasses or oxides. This irreproducibility has been related to the ester hydrolysis catalyzed by adsorbed water,[142] the ester being unable to spread on an adsorbed layer of its own hydrolysis products.

The same is believed to be true of the occasionally observed homeotropic alignment of LC esters of Schiff bases (SB) on glasses and some oxides (Al$_2$O$_3$, In$_2$O$_3$). This effect is normally only observed if the surfaces have previously been washed in acid. This alignment disappears when the substrate is fired and is not observed with pure LCs of other molecular structure. On dry substrates, LC esters, as opposed to liquid esters,[142] are flat on the surface due to the carboxylic group interacting strongly with the oxide.[151]

SBs are completely hydrolyzed during HPLC on silica columns[20] and are known to be very sensitive to moisture.[152] Hydrolysis of ester or SB LCs produce alkylbenzoic acid or alkylamine, respectively, both of which are known to induce homeotropic alignment. Surface hydrolysis leads to local concentrations higher than could be adsorbed from solutions; 1% concentrations of these substances in the LC are required to induce the same alignment. An indication that surface hydrolysis has occurred is the formation of defects that remain stuck to the substrate even after a heating cycle or the emptying and refilling of a cell. A related impurity induced homeotropic aligning effect is observed when LC layers are either left in air or submitted to light irradiation. Photooxidation of the LC forms oxyderivatives[45c] that induce homeotropic alignment. In the case of unsealed cells the perpendicular orientation proceeds from the outer edge.

II.1.10 Measurement of LC surface tension

This section is not devoted to a discussion of experimental surface tension measurements that would be found, for instance, in Ref. 121, but to the implications of the choice of one method. Capillary, du Nouy, Wilhemy methods imply the contact of LCs with surfaces.

From the preceding considerations of the LC–solid interaction one can understand the difficulties, generally underestimated, of obtaining reliable values; after long and careful studies it has been concluded that surface tension of MBBA is "impossible to measure".[113]

As LCs lie generally parallel to solid surfaces the above quoted method should give a value near that of γ_{ll}.

Only in the hanging drop method are the solid–LC interactions minimized and the γ_{LV} values should be obtained.[116] As LCs often orient perpendicular to the free surface the value of γ_s would be obtainable with a precision of about 5%. In fact, even in this method the solid-liquid interactions are predominant.[20]

The wide range of literature values may correspond to different aligning conditions and indicate an anisotropy $\Delta\gamma$ of about 10 erg, in agreement with theoretical considerations.[119]

II.1.11 Summary of Section II.1

As the solid surface tension, γ_s, is not measurable, one has sought to use, instead, the experimental γ_l value, which gives a rough expectation of the direction of LC alignment. This can only be exact when the ratio of the polar and dispersive components of both the solid and the LC are equal.

A quantitative description of a LCs alignment requires knowledge of the polar and dispersive parts of surface tension as polar interactions depend on a LCs dielectric anisotropy and may be predominant.

Determination of a LCs surface tension is, currently, not accurate enough to allow a precise comparison of substrate and LC surface tension. The majority of recent work suggests the validity of the FCK rule; much more work has to be done to get reliable values of a LCs surface tension. As long as experimental values of γ_{MBBA} continue to be found between 38 and 28 erg/cm^2, or γ_{SB} between 30 and 40, critical evaluation of the FCK rule, which requires a knowledge of γ to better than 1 erg/cm^2, is meaningless.

In our opinion there are no sound experimental data that invalidate this rule. Discrepancies indicate experimental error and we will suggest its use as a fair estimate of the expected alignment of a LC.

II.2 Elastic orientation on grooved surfaces

II.2.1 Geometrical factors

On high energy substrates ($\gamma_{SV} \geq 4 \times 10^{-2}$ J m^{-2}), LCs align parallel to the substrate. Sometimes, the flow of a LC drop will produce a nearly uniform alignment, albeit with many defects. This orientation occurs most easily when the LC is in its isotropic state. Very slow cooling[5] favors uniformity and good alignment is obtained on cooling in a magnetic field.[54]

These methods are impractical and uniformity is more easily obtained on grooved surfaces. Grooves are produced by rubbing (glass plates), unidirectional polishing, tangential evaporation, tangential ion-beam etching of oxides, or the formation of a grating on the substrate.[47,54]

Once the first interfacial layer is formed, the LC layer aligns through the nematic interactions at the shear plane; the LCs anchorage is fairly weak and defines a slippery surface. (see § II.3.1.) In these conditions, theoretical calculations of the elastic energy added to the LC bulk by a periodic surface deformation show[43] that the LC layer has an energy which is greater when the LC director is perpendicular to the groove direction d (but parallel to the substrate) than when the director lies in the direction of the groove.
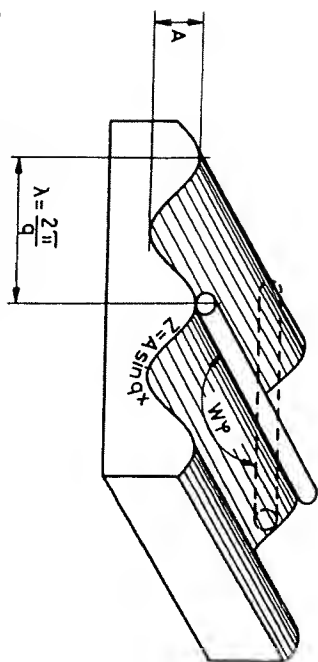
FIGURE 8   The sinusoidal model of a grooved surface. The LC molecules have higher elastic energy in the orientation perpendicular to the plane than parallel to it.

If the surface profile (Figure 8) is defined by the depth, A, of the grooves and their spacing $\lambda = 2\pi/q$

$$Z = A \sin qx \qquad U = \frac{K}{4} A^2 q^3$$

where K is the LC elastic constant. Table IX summarizes the profiles obtained by different grooving techniques and the related increases in energy for alignment parallel to the grooves. Photolithographically formed gratings allow the characterization of the periodic profile that influences the alignment. For 250 Å deep grooves uniform alignment of MBBA is obtained for

$$\lambda < 3.4\,\mu.$$

In general the ratio A/λ is smaller than 1.

TABLE IX

Estimated values of depth and spatial distribution of grooves on various substrates in the sinusoidal approximation

Surf. preparation	Depth A (Å)	Spacing (Å)	Energy[a] U J m^{-2}	Ref.
Rubbed glass	10	200	8×10^{-5}	43(a)
Polished glass	200	1000	2.4×10^{-4}	43(b)
(diamond pasic)				
Diamond pencil scratches	10000	<10 μ	15×10^{-7}	47
Evaporated SiO$_x$ 60°	100	200–400	6×10^{-4}	44(a)
Gratings	250	3200	1.2×10^{-4}	54

[a] U is the excess energy of the nematic liquid crystal aligned perpendicular to the grooves over its energy when it is aligned parallel to them. Calculated from $U = (1/4)K A^2 q^3$ assuming a unique elastic constant $K = 10^{-11}$ N.

If the different elastic constants of the LC are taken into account, calculations[47] indicate that for $K_{22} > 3K_{33}$ a metastable configuration exists where $\mathbf{n}$ is $\perp$ to $\mathbf{d}$ which cannot be observed, as $K_{22} \sim K_{33}/2$ for LCs.

Grooving does not influence homeotropic alignment provided the surface profile is symmetrical (Figure 9a'). Silanes or silicones deposited on grooved surfaces still induce homeotropic alignment.[20,157] Sawtooth profiles may produce an average tilted orientation in the bulk of a LC[44] (Figure 10), as will an unsymmetrical coating of the grooves.[108] Considering that the LC molecules are either lying parallel to the substrate or orthogonal to it[11b] three configurations of the LC may exist.[7] In the case of Figure 9a' the elastic energy of the LC layer is not a minimum and it will not be observed on a sinusoidal profile as described in Figure 8.
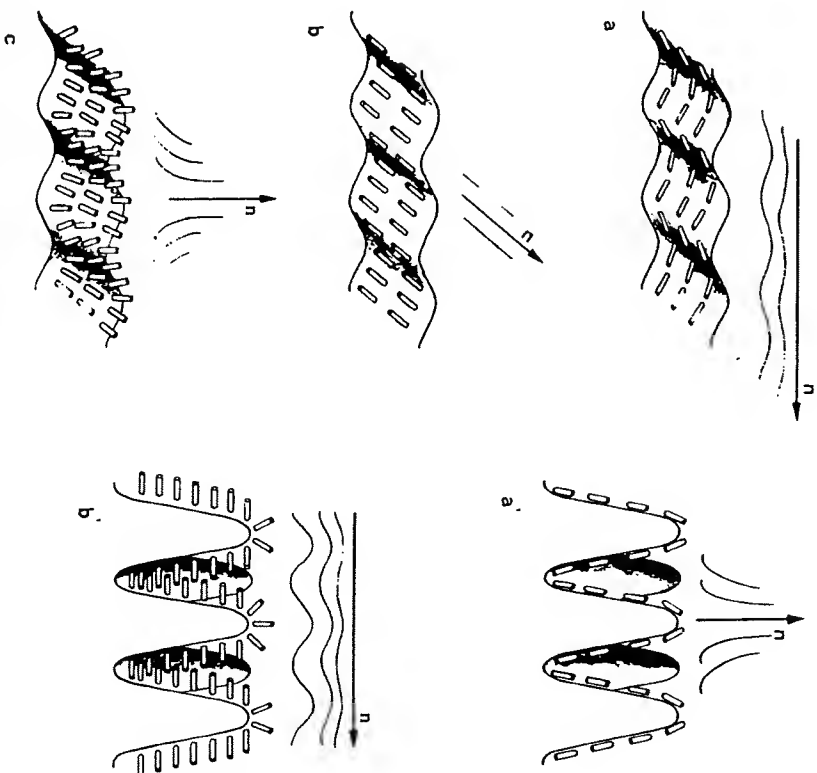

FIGURE 9   On grooved surface, parallel or homeotropic alignment may be observed depending upon the spatial period to amplitude ratio.
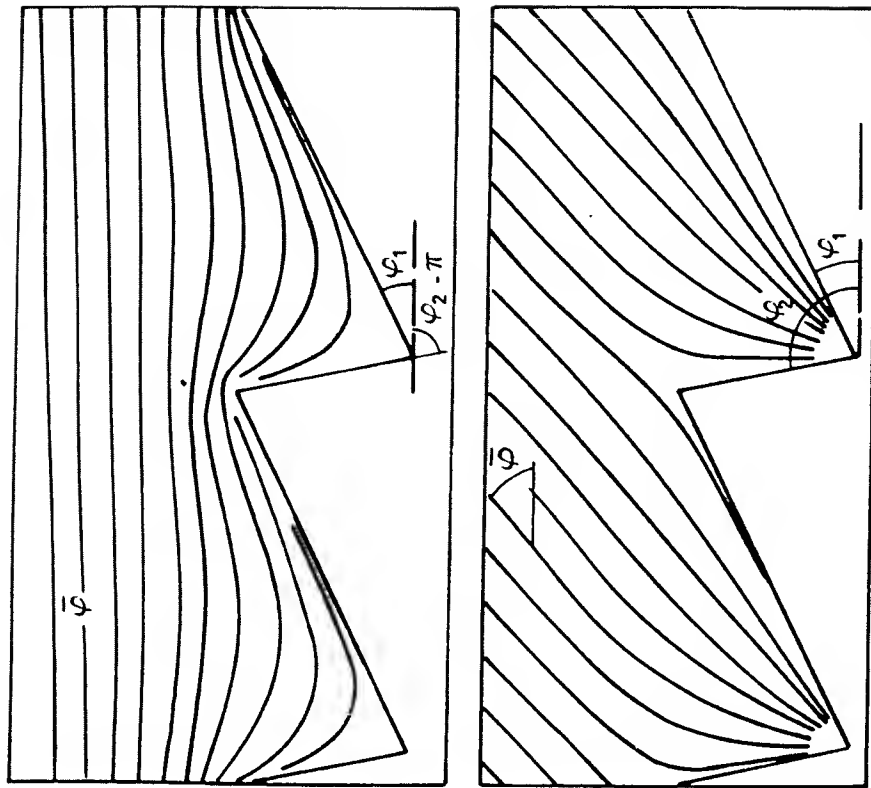
FIGURE 10   Unsymmetrical grooves may induce tilted alignment (case b) as evidenced by a rheographic model. (From Ref. 44). (a) $\phi = \phi_1$ on surface 1, $\phi = \phi_2$ on surface 2, $\bar{\phi} = 0$. (b) $\phi = \phi_1$ on surface 1, $\phi = \phi_2$ on surface 2, $\bar{\phi} = \phi_1[\pi/(\pi - \phi_2 + \phi_1)]$.

A three dimensional profile will create an alternation of peaks and valleys and constrain the LC to take the configuration of Figure 9b.

Depending on the width to depth ratio as compared to the molecular dimension the following situation may occur: if the substrate tension energy is high the molecules will lie flat on the surface but the bulk average will be homeotropic (similar considerations are found in Ref. 57). Lowering the surface tension energy by surfactant adsorption will orient the molecules perpendicular to the surface resulting in an homogeneous alignment.

Experimental evidence will be published later.‡ It requires that the depth of the hole be bigger than its width and the spacing of two pits is of the order of, at least, three molecular dimensions (i.e., 60 Å as LC molecules typically have length of 20 Å and width of 6 Å).

II.2.2 Mixed alignment

The alignment of LCs on parallel orienting surfaces with patches of a homeotropic aligning agent has been considered in § I.1.7.

Obliquely ($\theta > 15°$) evaporated SiO_x layers align LCs homogeneously. An additional tangential evaporation ($\theta < 15°$), which would otherwise produce a tilt angle of 25°, permits the selection of any orientation ($\pm3°$) of the LC molecules between 0° and 25°, as the asymmetry of the grooves increases. Deposition of a dense layer of a homeotropic aligning agent (see § II.1.8.) on a symmetrically grooved surface (either rubbed or obliquely evaporated) will not change the homeotropic orientation,[69,17] but as the first monolayer is oriented normal to the surface, a distortion exists in the LC layer. When such a homeotropic aligning layer is deposited on a nonsymmetric layer, producing a tilt angle ϕ, the complementary, $\phi + \pi/2$, tilt angle is observed (Figure 3).[5,20,157] †

II.3 Anchoring energies

II.3.1 Anchoring energies and the interfacial layer

The interactions of the LC molecules with the surface have to be taken into account when considering the LCs static deformation.

The energy of interaction, W_a, can be expressed phenomenologically as the sum of an isotropic energy term, W_0, an in-plane (twist or torsion) anchorage and an out-of-plane (azimuthal) anchorage:

$$W_a = W_0 + W_\phi + W_\theta, \tag{3.1}$$

where the angles are as indicated on Figure 11. The angular dependence of W_ϕ and W_θ can be described[153] by

$$W_\phi = B_\phi \sin^2 \phi, \tag{3.2}$$

$$W_\theta = W_0 + B_\theta \sin^2 \theta. \tag{3.3}$$

In the physical chemistry of surfaces, interfacial interactions are usually described by the surface tension of both phases.

When a liquid of surface tension γ_{LV} comes into contact with a solid of surface tension γ_{SV^e}, and interfacial layer builds up whose energy γ_{SL} (identical to W_a) is

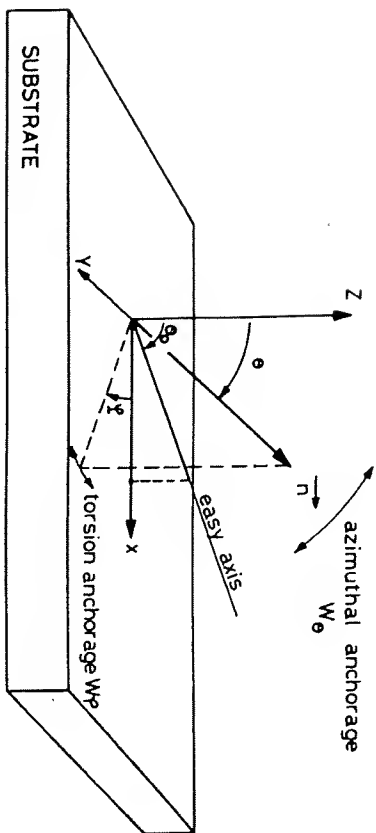$$\gamma_{SL} = \gamma_{SV^e} + \gamma_{LV} - W_a, \tag{3.4}$$

† Similar observations have been reported in Appl. Phys. Lett. 36, 144 (1980) by W. R. Heffner et al.
‡ F. Gharadjedaghi, "Liquid crystal alignment techniques producing controllable tilt angles" presented at the 4th Liquid Crystal Conference of Socialist Countries, October, 1981.

where γ_{SV}^0 is the solid surface tension at equilibrium with liquid saturated vapor (which is related to the solid-vacuum interface free energy γ_S and the adsorbed liquid layer surface pressure π_0 by $\gamma_{SV}^0 = \gamma_S - \pi^0$) and W_a is the adhesion energy which may be approximated[159] by

$$W_a = 2\sqrt{\gamma_{SV}^0 \gamma_{LV}}.$$ (3.5)

FIGURE 11 Definition of in-plane and azimuthal anchoring energies.

The solid surface energy, γ_S, is not directly measurable and depends on the surface preparation and history, but for inorganic substrates γ is calculated to be >0.2 J m^{-2}, in agreement with values obtained from heat of immersion measurements.[121] For polar liquids the surface pressure π_0 exceeds 0.1 J m^{-2} leading to γ_{SV}^0 values $>7 \times 10^{-2}$ J m^{-2} (Ref. 117) (the surface tension of an inorganic substrate covered with a water layer).

In the case of a liquid of $\gamma_{LV} = 3 \times 10^{-2}$ J m^{-2}, which is typical for LCs, the interfacial layer energy γ_{SL} is obtained from (3.4) and (3.5) giving $\gamma_{SL} = 8 \times 10^{-3}$ J m^{-2}.

The thickness of the interfacial layer is not known precisely but it extends over at least 100 Å in a resistive liquid with LC molecular dimensions.

From the interfacial energy profile as sketched in Figure 12, one sees that the anchoring energy varies with the distance from the surface.

The excess energy of the interfacial layer produces in nematic LCs a higher ordering which creates the smecticlike layer described in §II.1.6. As surface tension exerts a force normal to the substrate, there is no dependence of the interfacial energy on the in-plane orientation of the molecules.

II.3.2 *In-plane anchorage energy*

The torsion anchorage, W_ϕ, results from substrate nonuniformity which may be controlled, for instance, by uniform grooving of the surface (Figure 8), in
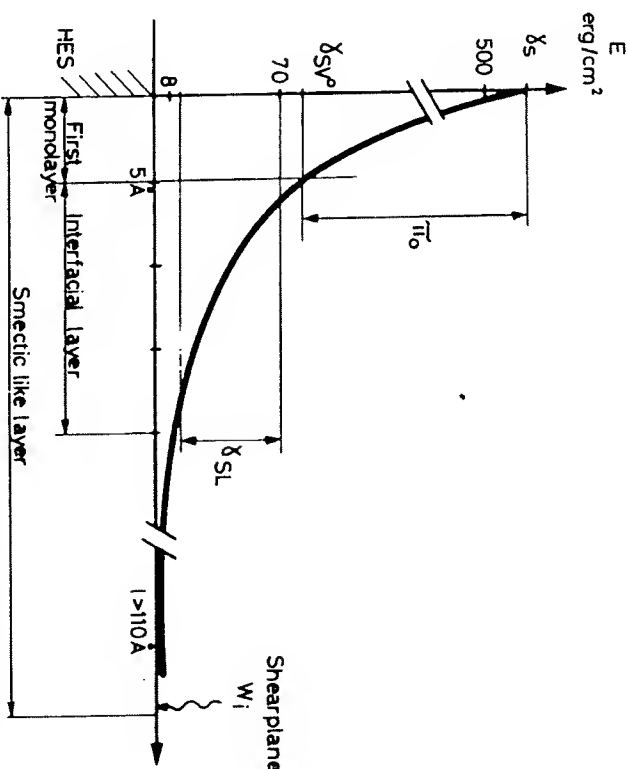
FIGURE 12 The surface-LC interaction energies vary with the distance to the surface. Close to the surface an ordered layer is related to the smectic organization. There exists a shearing plane at a distance where the energy of elastic deformation equals the excess energy due to surface interactions.

which case W_ϕ may be calculated (see §II.2; $W_\phi \equiv U$). W_ϕ may be roughly estimated from the width, h, of surface disclination lines[153]

$$W_\phi = \frac{\pi^2}{2} \frac{Kh}{d^2}$$

(where d is the LC layer thickness), or measured from the variation in twist angle of a twisted layer subject to a magnetic field.[155] As both experimental measurements and the elastic alignment theory relate to the alignment beyond the smectic layer, calculated and experimental values, as compared in Table X, show that the orders of magnitude are in fair agreement. In every case the torsion anchoring energy is higher than the bulk twist energy

$$W_{twist} = K \phi_T^2 / 2d \approx 10^{-6} \text{ J m}^{-2}$$

(ϕ_T = twist angle, See Ref. 158).

In a twisted nematic layer, minimizing the bulk free energy leads to the equilibrium condition $d\phi/dz$ = constant. In the vicinity of the substrate it is
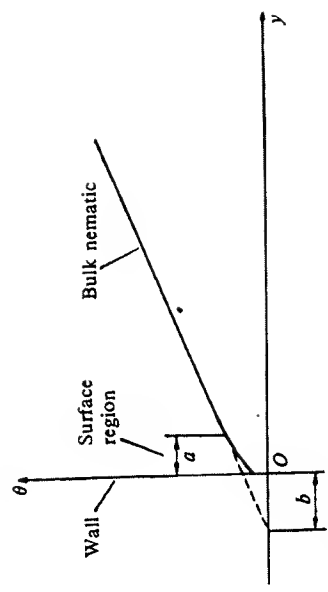
FIGURE 13 Definition of the "extrapolation length." "Weak in-plane anchoring corresponds to $b \ll d$. (From Ref. 156).

expected that this condition does not hold[156] and extrapolation of the linear variation of $\phi_{(z)}$, to $\phi = 0$ occurs at $z = -b$ (Figure 13). The "extrapolation length" $b = K/B\phi$ would in this case define the condition of strong anchoring. The twisted nematic layer behaves as if it had a thickness $d + 2b$; thus the anchoring is strong if $2b \ll d$.

The threshold voltage under applied electric field is given[157] by

$$V_{th} = \frac{\pi}{d + 2b} \sqrt{\frac{4\pi K}{\Delta\epsilon}} \left(1 - \frac{2K}{B_\phi d} \right). \qquad (3.6)$$

As the torsion anchoring energy on grooved surfaces may vary from 5×10^{-6} to 10^{-4} J m^{-2} (Table IX) the extrapolation length may reach 2μ for a typical LC cell ($d = 10^{-5}$ m) ($K = 10^{-11}$ N). In fact we have not found experimental evidence for the extrpolation length.

II.3.3 Azimuthal anchorage

As W_ϕ is independent of the interfacial interactions on uniform surfaces, the anchoring energy reverts to the energy of the azimuthal anchorage, which is equal to the difference between the interfacial energy when the LC is aligned parallel or perpendicular. Let $\xi(0)$ and $\xi(\pi/2)$ be the values of the physical property ξ in both orientations

$$W_\theta = W_0 + B_\theta \sin^2\theta = \gamma_{SL}(0) + \left[\gamma_{SL}\left(\frac{\pi}{2}\right) - \gamma_{SL}(0) \sin^2\theta \right]. \qquad (3.7)$$

TABLE X

Comparison of calculated and experimental values of the in-plane (torsion) anchoring energies

Substrate	W_ϕ calc (J m^{-2})[a]	W_ϕ exptl (J m^{-2})
Glass	...	5×10^{-6} (153)
Rubbed glass	8×10^{-5}	10^{-4} (153) 7×10^{-6} (155)
SiO$_x$ evap 30°	5×10^{-4}	10^{-3} (153)
Heptylamine on glass	...	$\sim 5 \times 10^{-5}$ (5)
Trimethyltrichlorosilane on glass	...	$\geqslant 5 \times 10^{-6}$ (5)

[a] $W_\phi \equiv U(\text{Table IX}) = 1/4\, K\, A^2\, \phi^3$ (1 erg/cm$^2 = 10^{-3}$ J m^{-2}).

In Eqs. (3.4) and (3.5), π_0, γ_{SL} and W_a are θ dependent, and

$$B_\theta = \gamma_{SL}\left(\frac{\pi}{2}\right) - \gamma_{SL}(0)$$

$$= \left[\pi_0(0) - \pi_0\left(\frac{\pi}{2}\right)\right] + \left[\gamma_{LV}\left(\frac{\pi}{2}\right)\gamma_{LV}(0)\right] + \left[W_a(0) - W_a\left(\frac{V}{2}\right)\right]. \quad (3.8)$$

There is no reliable data on these values for LCs. No account has been taken of the surface pressure in the literature. As on inorganic substrates LCs prefer to be parallel to the substrate, $\pi_0(0) > \pi_0(\pi/2)$ and the anisotropy is not expected to be large. The LC surface tension anisotropy, $\gamma = \gamma_{LV(0)} - \gamma_{LV(\pi/2)}$ is estimated to be $+4.5 \times 10^{-5}$ J m^{-2} for MBBA[66] and 5×10^{-6} J m^{-2} for 5 CB (102 a). The difference in adhesion energy W_a between the parallel and perpendicular orientation has been deduced from experimental data at the glass/MBBA interface to be 6.2×19^{-3} J m^{-2} (8 c) and is calculated to be 7.16×10^{-3} J m^{-2} for PAA on glass (102).

Thus the energy in the interfacial layer is mainly determined by the adhesion energy. From (3.8) one gets:

$$B_\theta = \gamma_{SL(\pi/2)} - \gamma_{SL(0)} \sim W_a(0) - W_a\left(\frac{\pi}{2}\right) = 6 \times 10^{-3} \text{ J m}^{-2}.$$

This large difference in the surface energy means that the orientation of the interfacial layer cannot be modified by elastic deformation of the LC where the energy is at most 10^{-5} J m^{-2}. In this case,[138] one should not minimize the bulk plus surface energy, but minimize the bulk energy and require the boundary conditions to be satisfied at the surface.

Writing the LC layer energy as

$$F = \frac{1}{2} W_a \theta^2_{(0)} + \int_0^d \frac{1}{2} K \left(\frac{d\theta}{dz}\right)^2 dz$$

is tantamount to putting a flea on an elephant and minimizing the weight of the flea to lower the weight of the combined system. A LC layer of thickness d, homeotropically oriented and subject to a magnetic field directed parallel to the substrate will change its orientation beyond a distance d_c:

$$d_c = \frac{3K}{2(\gamma_\perp - \gamma_\parallel)} \quad (3.9)$$

as observed[138] on a homogeneously aligned drop of PAA deposited in a hole drilled in a crystal sheet, and subjected to a magnetic field perpendicular to the substrate. Azimuthal anchoring energies are either estimated from surface disclination lines[153] or measured by magnetic deformation of homeotropically

TABLE XI

Experimental values of the angular coefficient B_θ of azimuthal anchoring energy W_θ ($W_\theta = W_0 + B_\theta \sin^2\theta$)

Substrate	LC	B_θ (10^{-6} J m^{-2})	Method[a]	Ref.
Air				
SiO$_x$ (30° + 5°)	5CB	4	DA	120(a)
Glass + R,N'Me$_3$X$^-$	6CB	2.1	Δn	109
Glass + NH$_2$C$_n$H$_{2n+1}$	MBBA	3	MD	75
Glass + NH$_2$-C$_7$H$_{15}$	MBBA	2	MD	155
Glass + lecithin	MBBA	2.6	SD	5(a)
Glass + lecithin	MBBA	3	MD	75
Glass + DMOAP	MBBA	6	MD	75
In$_2$O$_3$ + DMOAP	MBBA	6	MD	75
In$_2$O$_3$ + lecithin	MBBA	10	MD	75
In$_2$O$_3$ + lecithin	MBBA	6	MD	75
In$_2$O$_3$ + NH$_2$C$_{16}$H$_{33}$	MBBA	3.5	MD	75

[a] Method: DA, differential anchoring: Δn, birefringence: MD, magnetic deformation: SD, surface disclination. The order of magnitudes of B_θ compared to the experimental surface tension anisotropy. MBBA: $\gamma_\parallel - \gamma_\perp \sim 4.5 \times 10^{-5}$ J m^{-2} [Ref. 75(b)]: 5CB: $\gamma_\parallel - \gamma_\perp \sim 5 \times 10^{-6}$ J m^{-2} [Ref. 120(a)].

oriented layers where (3.9) should apply. The B_θ values obtained are weak and comparable to the LC surface tension anisotropy (Table XI). This difference between calculated and experimental values would correspond to a deformation of the LC layer where the LC is not affected by the surface potential and $B_\theta \sim \gamma(0) - \gamma(\pi/2)$.

On inorganic layers where a LC would normally align parallel to the substrate, even though the anchorage is strong, weak interactions are observed as the perturbed part of the nematic layer interacts with its smecticlike interfacial layer. The same situation is probably observed on most adsorbed surfactant layers. With $B_\theta \approx 5 \times 10^{-6}$ J m^{-2} the anchorage parameter of Ref. 158

$$\lambda = \pi \frac{K}{B_\theta d}$$

is about 1 for a LC with $K \approx 10^{-11}$ N and a cell thickness of $d = 10\mu$.

Thus one may wonder whether it would be possible to observe weaker anchorage than now known. On polymeric films surface interactions are strongly reduced and the interfacial layer may disappear, but very often homeotropic alignment is observed on these surfaces.

II.1.4 Conclusions

As phrophesized sixty years ago[23]:

"Les actions auxquelles obéissent les liquides anisotropes, qui se révèlent par des structures si variées, pourront sans doute plus tard se résumer en quelques lois très simples."

Bien que ces dernières ne soient pas connues, on est en droit de penser, d'après les observations très nombreuses recueillies jusqu'à ce jour, qu'elles feront jouer un rôle très important aux actions superficielles qui règlent l'orientation du liquide au voisinage de la surface, dans la couche capillaire, et les distingueront nettement des actions intérieures qui fixent l'orientation du liquide par rapport à lui-même dans toute l'étude de sa masse. Aux premières se rattachent par exemple les plages orientées à la surface du verre: aux secondes les coniques focales, les fils."

Mastering the alignment of LCs requires the control of the smecticlike interfacial layer. In addition to the difficulties of obtaining uniform and clean substrates, pure LC and well defined aligning layers free of solvents and ionic contamination, LC molecular structure gives rise to complicated interactions. Constituted of an aromatic core having strong dispersive interactions with the substrate, an alkyl chain tending to orient perpendicularly to the surface as the chain length increases, and a polar group which may counteract the other part of the molecules minimum energy, LC molecules open wide fields to speculation.

Theoretical expectations are summarized in Table (XII). Nevertheless, even if all aspects of LC orientation are not under control, as is also the case for the physical chemistry of surfaces, reproducible and well defined alignment can be obtained, as described in the last paragraph.

In general, inorganic substrates lead to nonuniform parallel alignment, the conditions that lead to homeotropically aligned LCs on these surfaces have not been defined. Rubbing will provide uniformity; it is best achieved on soft polymeric layers. Homeotropic alignment is observed in the absence of interaction with the surface as in suspended films, on low energy polymers and on adsorbed surfactant layers. The very first organized layer reaches its equilibrium slowly and determines the final nematic crystal structure.

III RECOMMENDED PROCEDURES

Alignment problems arise frequently in laboratory experiments where LCs and temperatures vary. It is therefore desirable to use procedures which have been well tested. The use of good alignment layers allows experiments involving a LCs physical properties to be performed without the use of cumbersome magnets.

The success of any aligning process depends upon the substrate and the cleaning procedures employed. The alignment of a LC may be studied on metal or crystal surfaces, but it is more usual to employ transparent substrates.

Glass, quartz, silicon coated glass, or transparent conducting coatings (SnO_2, In_2O_3)—patterned or otherwise—are most frequently employed. One should be aware of the many varieties of glass compositions available and the various manufacturing methods (pulled, floated, fire polished) which lead to

TABLE XII

Alignment expected from substrate/LC interaction characterized by the dispersive and polar components of the solid and LC surface tension

Surface \ Liquid crystal	Surf. state	$\gamma_{el} < \gamma_s$		$\gamma_{el} > \gamma_s$	
		$\Delta\epsilon > 0^a$	$\Delta\epsilon < 0$	$\Delta\epsilon > 0$	$\Delta\epsilon < 0$
Surf. tension $\gamma_s = \gamma_s^p + \gamma_s^d$	Smooth	$\perp^b$	$\times^b$	No cases	
$\gamma_i^p \gg \gamma_i^d$				polar surfaces ($\gamma_i^p \gg \gamma_i^d$) have $\gamma_{el} > \gamma_d$	
Activated oxides diacids	Sym grooves	$\perp$	$=$	have	
	Unsym grooves	⟂̸	⟂̸	⟂̸	
	Tridimensional^c pit array	$=$	$\perp$	$\perp$	
$\gamma_i^p \gg \gamma_i^d$	Smooth	$\times$	$\times$	$\perp^d$	$\perp^d$
Humid oxides polymers fatty deriv.	Sym grooves	$=$	$=$	$\perp$	$\perp$
	Unsym grooves	⟂̸	⟂̸	⟂̸	⟂̸
	Tridimensional^c pit array	$\perp^d$	$\perp^d$	$=$	$=$

ᵃ $\Delta\epsilon$ gives an indication of the LC polarity.
ᵇ This case is not experimentally very well documented.
ᶜ Regularly repeating tridimensional array of peaks and valleys.
ᵈ Homeotropy due to tridimensional array does not depend upon LCs nature while that due to absence of interaction does.
ᵉ ⟂̸ and ╫ = tilted alignment.

different interactions with the LC to be aligned. The use of an acid bath to clean the substrate changes its properties towards certain classes of LCs. These considerations are not too important if the substrate is to be coated with a polymeric or oxide layer, but they are essential when silanes or surfactants are to be employed as aligning agents. More reproducible results are always obtained on an underlying coating.

The following methods have been widely used with success and give good results with most combinations of substrate and LC.

III.1 Cleaning

Cleaning of solid substrates is still an art despite the considerable amount of work done on it.[160] Our studies use either a detergent bath or dipping in boiling sulfuric acid followed by thorough 18 MΩ water rinse and centrifuge drying.

Other methods may be found in the literature, as for instance in Ref. 159. A very important step in any cleaning procedure is the drying, which has to be effected rapidly, i.e., under a high pressure stream of gas.

III.2 Parallel alignment

Alignment by the rubbing of a substrate has been reviewed. In the laboratory, uniform alignment will be difficult to obtain reproducibly on every substrate. Industrial processing employs sophisticated machines. Rubbing by hand with a woven material or a polishing paste can only be expected to give uniform and reproducible results on soft substrates (glass or polymers).

III.2.1 Rubbed PVA

Thin polymeric films are best deposited by spin coating. A spinner may easily be constructed for laboratory uses. Polyvinyl alcohol (PVA) is commercially available in different grades (Wacker Polyviol®), but it appears that its aligning properties are not related to the grade used. We currently use the M 13/140 grade, which is very soluble and produces uniform films.

An aqueous solution (3%) is filtered on 0.5μ millipore filters and deposited on a spinning (4000 rpm) substrate at room temperature. The deposited film (d ~ 1000 Å) is dried at 80°C for 30 min and subsequently rubbed with a textile cloth. Uniform alignment with a very low tilt angle is obtained on all substrates and with most LCs.

III.2.2 Rubbed polyimide

Although PVA forms good aligning layers it is water and temperature sensitive. Polyimide is a very stable polymer. Films may be formed on a solid substrate from a monomer solution of an acid anhydride and a polyamine. Such solutions in N-methylpyrrolidone are commercially available (Rhône Pou-

lenc, Nolimide 32). The deposition of a uniform film is more difficult than with PVA.

Spin coating is effected as described above from a 1/10 diluted solution and the resulting deposit dried at 80°C for 30 min. The soft prepolymer is then rubbed. Polymerization is achieved by curing in two steps, 130°C, 30 min, followed by 200°C, 30 min.

III.2.3 SiOₓ evaporation

If an evaporator is available, SiOₓ evaporation is the easiest way to obtain stable, uniform, reproducible alignment in the laboratory, provided that the substrate is flat and homogeneous. Uniform alignment with varying tilt angles may be obtained by variation of the angle between the substrate plane and the direction of the incident beam. Parallel alignment is obtain for a 30° angle.

Pure silicon monoxide (Balzers 99.99) is evaporated by techniques which are well known[161]; boat temperature 1300–1400°C, $p \cong 10^{-4}$ mm Hg, air bleeding. Typical thicknesses are 200–300 Å. (MgF₂ may also be used.)

III.3 Homeotropic alignment

There are at present no entirely satisfactory methods to obtain easy, reproducible homeotropic alignment free of complications (short lifetime, conductivity increase, etc.); for experimental evaluation the following methods give good results.

III.3.1 Lecithin (DMOAP)

The easiest way to obtain a homeotropically aligned LC layer is to sandwich it between lecithin coated layers. A solution of natural egg lecithin (Merck 5331) in a volatile solvent (e.g., alcohol) is used and the substrates are either spin-coated or dipped in the solution. The concentration is unimportant but the use of a dilute (1%) solution avoids the formation of spots. The coating is rinsed with the solvent and dried at 80°C for 30 min.

Alignment of most LCs is obtained in a direction orthogonal to the substrate plane without any tilt. There is no variation of the orientation with temperature, but the LC conductivity is increased. With the same technique DMOAP [dimethyloctadecyl-3-(trimethoxysilyl)propylammonium chloride, Petrarch 09745] gives similar results and drawbacks but is somewhat more substrate sensitive.

III.3.2 DMCS

For the alignment of positive LCs (the technique fails in the case of many negative Δε LCs) a polymethylsiloxane, insulating, homeotropically aligning layer may easily be formed on the substrate from a Dimethyldichlorosilane

(Fluka 46140) solution 10% in toluene) by dipping the plate for 15 min at room temperature. The coating is rinsed with isopropyl alcohol and cured at 100°C for 30 min.

III.4 Tilted alignment

III.4.1 *Tangentially evaporated SiO_x*

As previously stressed, tilt angle is a bulk average, depending on both the surface state and the LCs elastic constants. It is thus difficult to know with precision the tilt angle one will obtain with different LCs sandwiched between the same plates. A tilt angle of 15° to 30° will be obtained on tangentially evaporated SiO_x. The evaporating conditions are the same as in § III.2.3.

III.4.2 *Crossed evaporation*

To obtain angles between 0° and 30° it is possible to deposit a thin layer of tangentially evaporated SiO_x on top of a 30° evaporated layer (low angles) or the reverse (high angles). Care must be taken to rotate the substrate by 90° between each evaporation as the nematic director is oriented perpendicular to the evaporation direction for tangentially evaporated layers.

III.4.3 *"Tilted homeotropic" alignment*

To obtain a slight tilt angle from the direction normal to the substrate a homeotropic aligning agent (e.g., Lecithin or DMOAP) is combined with one of the above methods (4.1., 4.2). The procedure is as outlined in § III.3.

Acknowledgments

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INDEX